INORGANIC CONDENSATION REACTIONS
I. STANNOSILOXANE FORMATION

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ABSTRACT

INORGANIC CONDENSATION REACTIONS

I. STANNOSILOXANE FORMATION

by Curt Thies

A series of stannosiloxane compounds has been prepared by the condensation of sodium triphenylsilanolate with various organotin chlorides in benzene. Infrared and elemental analyses were employed to characterize the reaction products.

The stoichiometry of the reaction of sodium triphenylsilanolate with several organotin chlorides in benzene has been established. It has been found that such reactions go rapidly to completion and are free of significant side reactions. This implies the reaction of pure $(NaO)_2Si\phi_2$ with organotin dichlorides in an aprotic solvent will yield high molecular weight stannosiloxane polymers having a regular alternating (-Si-O-Sn-) structure.

Several stannosiloxane polymers have been prepared by the <u>in</u> <u>situ</u> condensation of $(NaO)_2Si\phi_2$ with dibutyltin dichloride. The polymers were not fully characterized, but it has been established that the polymerization process is rapid. Highly purified $(NaO)_2Si\phi_2$, which is soluble in absolute ethanol, has been isolated and will be used in future stannosiloxane polymerizations.

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By

Curt Thies

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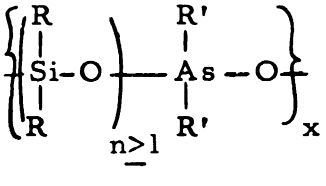
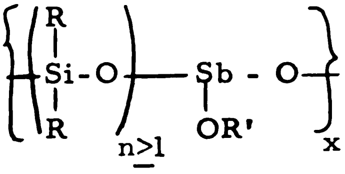
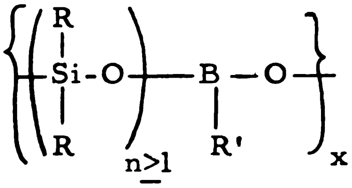
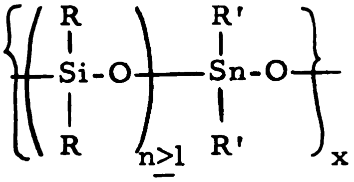
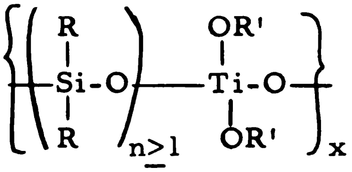
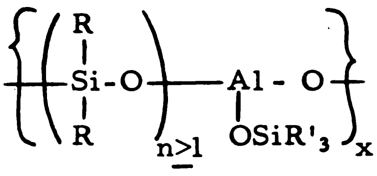
I. INTRODUCTION

A. General

In recent years a need has arisen for materials having both stability and flexibility at high temperatures. This has stimulated work on polymers containing inorganic elements in the backbone structure. The organosiloxane polymers have served as a starting point for much of the work since they combine good thermal stability with mechanical versatility (1). The use of these polymers at extremely high temperatures is limited principally because of decomposition and a tendency to form cyclic structures under such conditions (2). It has been proposed this tendency would be reduced by replacing some of the Si-O units in the polymer chain with Ti-O, Al-O, or generally, metal-oxygen units (3). Several authors have postulated the more ionic bond character caused by the introduction of metal-oxygen units would itself increase the thermal stability of the polymer structures (3, 4). For these reasons many attempts have been made to prepare organometallosiloxane polymers containing silicon and various elements from the second, third, fourth, and fifth groups of the periodic table (5, 6). All of these have been prepared by simple condensation processes as few monomers are known which polymerize by addition reactions (7). Proposed structures and nomenclature for several polymers which have been synthesized are listed in Table I.

Although high molcular weight organosiloxane polymers (the silicones) have been prepared, most organometallosiloxane polymers reported to date have had number average molecular weights ($\overline{M}_n$) ranging from 1000 to 5000. The low $\overline{M}_n$'s are believed due to various side reactions which in part lead to formation of cyclic structures. As no quantitative studies have been carried out to establish the course and kinetic mechanisms of

Table I. Postulated Structures of Reported Organometallosiloxane Polymers

Polymer	Structure	Reference
Organoarsonosiloxane	 $\left\{\left(\underset{R}{\overset{R}{\mathrm{Si}}}-O\right)_{n\geq 1}-\underset{R'}{\overset{R'}{\mathrm{As}}}-O\right\}_x$	8
Organoantimonosiloxane	 $\left\{\left(\underset{R}{\overset{R}{\mathrm{Si}}}-O\right)_{n\geq 1}-\underset{OR'}{\mathrm{Sb}}-O\right\}_x$	9
Organoborosiloxane	 $\left\{\left(\underset{R}{\overset{R}{\mathrm{Si}}}-O\right)_{n\geq 1}-\underset{R'}{\mathrm{B}}-O\right\}_x$	10
Organostannosiloxane	 $\left\{\left(\underset{R}{\overset{R}{\mathrm{Si}}}-O\right)_{n\geq 1}-\underset{R'}{\overset{R'}{\mathrm{Sn}}}-O\right\}_x$	4, 11, 12, 13, 14
Organotitanosiloxane	 $\left\{\left(\underset{R}{\overset{R}{\mathrm{Si}}}-O\right)_{n\geq 1}-\underset{OR'}{\overset{OR'}{\mathrm{Ti}}}-O\right\}_x$	12
(Triorganosiloxy)aluminosiloxane	 $\left\{\left(\underset{R}{\overset{R}{\mathrm{Si}}}-O\right)_{n\geq 1}-\underset{OSiR'_3}{\mathrm{Al}}-O\right\}_x$	3

the condensation reactions, the purpose of this study was to investigate a prototype inorganic condensation reaction. The stannosiloxane system was selected for the following reasons:

1. Organotin monomers are readily available.
2. The Sn-C bond is stable (15).
3. Organotin compounds can be easily purified and handled without elaborate techniques.
4. It has been established Si-O-Sn bonds can be formed (16, 17).
5. Several qualitative studies of low $\bar{M}_n$ stannosiloxane polymers have been made (4, 11, 12, 13, 14).
6. Organotin additives are known to increase thermal stability of some organosiloxane polymers (4).

Since no quantitative studies of stannosiloxane reaction systems have been made, the present investigation was undertaken to obtain stoichiometric and, if possible, rate data for the formation of well-defined compounds. The results will later be applied to polycondensation reactions.

B. Principles of Polycondensation

Polycondensation occurs when substances with two or more reactive groups undergo a simple chemical reaction with each other. The first reaction step produces a dimer which by subsequent reactions with additional monomers gives a trimer, tetramer, etc. However, this isn't the only possibility. Two dimers may react to form a tetramer, two trimers may unite to form a hexamer, etc. This process eventually leads to a high polymer as shown in the following simplified scheme:

$$\mathrm{X{-}R{-}Y + X{-}R{-}Y \longrightarrow X{-}R{-}R{-}Y + XY}$$

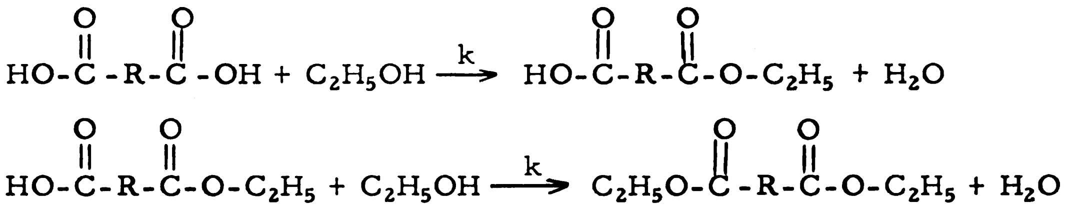
$$\mathrm{X{-}R{-}R{-}Y + X{-}R{-}Y \longrightarrow X{-}R{-}R{-}R{-}Y + XY}$$

$$\mathrm{X{-}(R)_m{-}Y + X{-}(R)_n{-}Y \longrightarrow X{-}(R)_{m+n}{-}Y + XY}$$

The following discussion of the above process is based on Flory's classical treatment of polycondensation reactions (18).

A fundamental assumption of polycondensation theory is that the reactivity of a functional group is independent of chain length and hence, all functional groups in the system react at random. It has long been known reaction rate constants for a homologous series of monomeric organic compounds are independent of chain length except for very short chains. This is illustrated by the results obtained for the acid catalyzed condensation of mono- and dibasic acids with ethanol shown in Table II (18, 19). Except for the first members of both series, there is no significant variation of the rate constant with chain length. Likewise, differences in the rate constants for esterification of mono- and dibasic acids disappear as chain length separating the carboxyl groups increases.

Perhaps more important is the observation that the same rate constant can be applied to each of the consecutive steps in the conversion of the dibasic acid to a diester:



$$HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + C_2H_5OH \xrightarrow{k} HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}C_2H_5 + H_2O$$

$$HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}C_2H_5 + C_2H_5OH \xrightarrow{k} C_2H_5O\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}C_2H_5 + H_2O$$

No variation in k was observed throughout the course of the reaction. Similar results were obtained from hydrolytic studies of ethylene glycol di and triacetate as well as diethyl succinate. This demonstrates that ordinarily the reactivity of a functional group in a polyfunctional molecule can be assigned a definite value which does not change during the course of a reaction. Neighboring substituents may markedly affect reactivity, but the reaction of one functional group will not noticeably affect its influence on the other. Any effect of this nature decreases rapidly with the distance of separation in the molecule. These generalizations are for reactions which do not involve interaction between a pair of charged

Table II. Rate Constants for Esterification of Homologous Series of Monobasic and Dibasic Acids (18, 19)

Chain Length	$k_A \times 10^4$ at 25°C (Esterification of monobasic acids)*	$k_B \times 10^4$ at 25°C (Esterification of dibasic acids)*
1	22.1	---
2	15.3	6.0
3	7.5	8.7
4	7.4	8.4
5	7.4	7.8
6	----	7.3
8	7.5	---
9	7.4	---
Higher	7.6	---

*All rate constants express in (gram equivalents/liter)$^{-1}$sec^{-1}.

reactants. When charged species are involved, functional group reactivity may not be entirely independent of the status of other groups in the molecule.

Although the reaction rate of a functional group does not depend on the size of the molecule to which it is attached, this does not necessarily mean the rate is independent of size in polymers of high molecular weight. Several arguments for decreased reactivity with increased chain length have been made based entirely on the mechanics of interaction of two functional groups attached to large molecules. It was postulated the collision rate for large molecules must be small because of their low kinetic velocity and the high viscosity of the liquid medium would further reduce reactivity. Shielding of the functional group within the coiled chain was offered as another reason for lowered reactivity.

However, Flory has shown from a theoretical viewpoint that none of these arguments is valid. Large molecules are known to diffuse slowly, but this must not be confused with the collision rates of the functional group. Mobility of this group is much greater than the macroscopic viscosity would indicate. Even though its range is limited by attachment to the polymer, the reactive group may diffuse readily over a considerable region through rearrangements in the conformations of nearby segments of the chain. Its actual oscillations against immediate neighbors may occur at a frequency comparable to, or not much less than, that existing in simple liquids. Consequently, the actual collision frequency will be essentially independent of the mobility of the molecule as a whole and the macroscopic viscosity.

As Rabinowitch and Wood have shown (20), a pair of functional groups which diffuse together in the liquid state may undergo repeated collisions before diffusing apart. A decrease in the diffusion rate will prolong this series while proportionately increasing the time between successive encounters. In this way decreased mobility will change the time distribution of collisions experienced by a functional group, but it shouldn't significantly affect the collision rate averaged over a period that is long compared to the time for diffusion from one partner to the next. Even if it does, the duration of the collided state will be proportionately increased with the net effect that concentration of pairs of functional groups close enough for reaction (assuming the necessary activation energy is available) is independent of mobility.

The independence of reaction rate and molecular size may be qualitatively shown from transition state theory where the rate constant, K is given by

$$k = K^{*} \, (k T/h) \qquad (1)$$

and k = Boltzmann's constant, T = absolute temperature, h = Planck's constant, and K^{*} = equilibrium constant for the activated complex. For a bimolecular reaction

$$K^{*} = F_{ab}^{\;*}/F_aF_b \quad \exp\,(-E_0/kT) \qquad (2)$$

where $F_{ab}^{\;*}$, F_a, and F_b are the partition functions of the activated complex and the two reactants respectively; E_0 is the energy of the activated complex at absolute zero. If the complexity of one or both of the reactants is increased, $F_{ab}^{\;*}$ and the product F_aF_b change by nearly identical factors for the added degrees of freedom unless this increase alters the molecule in the immediate vicinity of the functional group. Thus, mobility within the liquid will not affect the equilibrium

$$\text{reactants} \;\rightleftarrows\; \text{activated complex.}$$

The rate of reaction is proportional to the activated complex concentration so it will not be influenced by mobility of the molecules, diffusion rate, or viscosity.

Exceptions to these conclusions result when molecular mobility is exceedingly low or when the reaction rate constant is exceptionally large and the mobility is low. In such cases equilibrium concentration of reactant pairs may not be maintained and the reaction would become diffusion controlled. As condensation polymerizations generally involve reactions of moderate rate, the concentration of reactant pairs should be readily maintained even at highest molecular weights and viscosities.

The only remaining argument for low polymer reactivity is the belief that the reactive group of a large polymer will be shielded by the coiling of the chain. This may be a real effect in very dilute solutions where the randomly coiled polymer molecules are more or less independent of each other. However, in more concentrated solutions the polymer chains are randomly intertwined. A reactive group has no preference for units in its own chain and will generally be encircled by units of other molecules. These units act as diluents and are taken into account by writing the rate expression in terms of concentrations of functional groups participating in the reaction per unit volume.

Flory verified his theoretical arguments for the independence of the reaction rate and molecular size by comparing the kinetics of homogeneous monofunctional and bifunctional esterification reactions (21). Assuming the velocity constant, k, is the same for all functional groups, the rate expression for uncatalyzed polyesterification is

$$-d\,[\mathrm{COOH}]/dt = k\,[\mathrm{COOH}]^2[\mathrm{OH}] \qquad (3)$$

where concentrations are expressed as equivalents of the functional groups. Assuming equal carboxyl and hydroxyl concentrations, this may be integrated to give:

$$2kt = \frac{1}{c^2} - \mathrm{Const.} \qquad (4)$$

where c = reactant concentration at time t.

By defining p as the fraction of functional groups initially present that have undergone reaction at time t, equation 4 can be replaced by

$$2kt = \frac{1}{(1-p)^2} - \text{Const.} \tag{5}$$

where $c = (1 - p)\ c_0$.

Flory found that data for both monofunctional and polyfunctional esterifications fit equation 5 except during the initial stages of the reaction. The exact cause for this behavior during the earlier stages of the reaction is not important since it is characteristic of simple esterifications as well as those which lead to polymer formation. The similarity in mono- and polyesterifications is direct evidence for nondependence of reactivity on molecular size.

The principle of equal reactivity of all functional groups is extremely important because it allows the kinetics of a polycondensation process to be treated as a simple chemical reaction and makes possible the analysis of polymer constitution using simple statistical methods (18). It also permits calculation of the number average degree of polymerization, $\overline{X}_n$, from the extent of reaction p.

If a polycondensation reaction is free of side reactions and involves pure bifunctional monomers of the type X-Y, or equivalent proportions of X-X and Y-Y, the number of unreacted groups is equal to the number of molecules present in the system. The number of molecules per unit volume is given by $c_0(1-p)$. Define a structural unit as each residue from an X-Y, or X-X and Y-Y unit so that the total number of structural units is equal to the total number of bifunctional monomers initially used. $\overline{X}_n$ will then be given by

$$\overline{X}_n = \frac{\text{Number of units}}{\text{Number of molecules}} = \frac{c_0}{(1-p)c_0} = \frac{1}{(1-p)} \tag{6}$$

The number average molecular weight is

$$\bar{M}_n = M_0/(1-p) \tag{7}$$

where M_0 is the mean molecular weight of a structural unit.

Equations 6 and 7 assume reactive groups X and Y are present in equivalent amounts and that no side reactions occur. $\bar{M}_n$ values calculated for cases where these stringent conditions are not met will be erroneous. Flory (18) has developed a relation between theoretical $\bar{M}_n$ values and nonequivalence of reactants, monofunctional reactants, or imbalance in the stoichiometric proportions. Assume a small amount of a reactant Y—+—Y is added to either pure monomer X—Y or stoichiometric proportions of X—X and Y—Y. Y—+—Y may or may not be identical with Y—Y. Define N_x as the total number of X groups initially present, N_y as the total number of initial Y groups, and r as the ratio N_x/N_y so that the total number of units is

$$(N_x + N_y)/2 = N_x\left(1 + \frac{1}{r}\right)/2 \tag{8}$$

while the total number of ends of chains is given by

$$2N_x(1 - p) + (N_y - N_x) = N_x[2(1-p) + (1-r)/r] \tag{9}$$

The total number of molecules is half the total number of chain ends so that $\bar{X}_n$ is expressed by

$$\bar{X}_n = \frac{\text{Number of units}}{\text{Number of molecules}} = \frac{1 + r}{2r(1-p) + 1 - r} \tag{10}$$

This relation is applicable to polymers containing small amounts of a monofunctional reactant Y—+ if r is defined as $N_x/(N_x + 2N_{Y+})$.

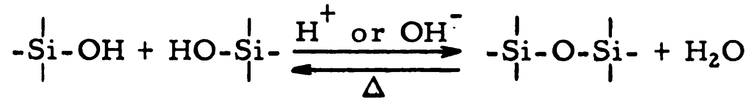
Assuming a complete reaction ($p = 1$), theoretical maximum values of $\bar{X}_n$ can be calculated for the case where small amounts of monofunctional reactants are present or where stoichiometric imbalance of the bifunctional monomers exists. For p = 1, equation 10 becomes

$$\bar{X}_n = \frac{1 + r}{1 - r} \qquad (11)$$

A plot of $\overline{X_n}$ for various r values in Figure 1 shows $\overline{X}_n$ is markedly affected by small deviations from r = 1. This graphically shows why high molecular weight linear condensation polymers are formed only from reactions involving extremely pure bifunctional monomers present in stoichiometric proportions. If these stringent conditions are not met and if side reactions occur which create monofunctional units or destroy the chain growth process, it will not be possible to synthesize high polymers by a simple condensation process.

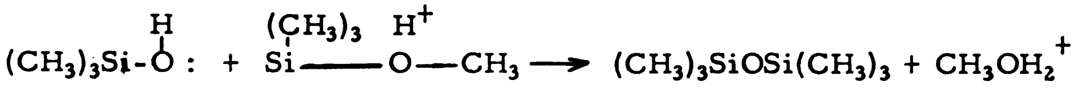
C. Organosiloxane Formation

Since organosiloxane polymers are prototypes of organometallo-siloxane polymers, the mechanism of siloxane bond formation is of interest in the present study. These linkages can be formed by the condensation of organosilanols



$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}- \underset{\Delta}{\overset{H^+ \text{ or } OH^-}{\rightleftharpoons}} -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O$$

This reaction has been studied by Grubb (22) who examined the acid and base catalyzed condensation of trimethylsilanol in methanol at 25°C. The proposed mechanism for acid catalyzed condensation is



$$(CH_3)_3Si-\overset{H}{\overset{|}{O}}: + \overset{(CH_3)_3}{\overset{|}{Si}}\text{——}\overset{H^+}{O}\text{—}CH_3 \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + CH_3OH_2^+$$

where all protonated species were assumed to be in non-rate determining equilibrium. Since the concentration of $(CH_3)_3Si\overset{H^+}{O}CH_3$ is proportional to acid catalyst concentration, the rate is first-order with respect to the catalyst. A similar mechanism was proposed for base catalyzed

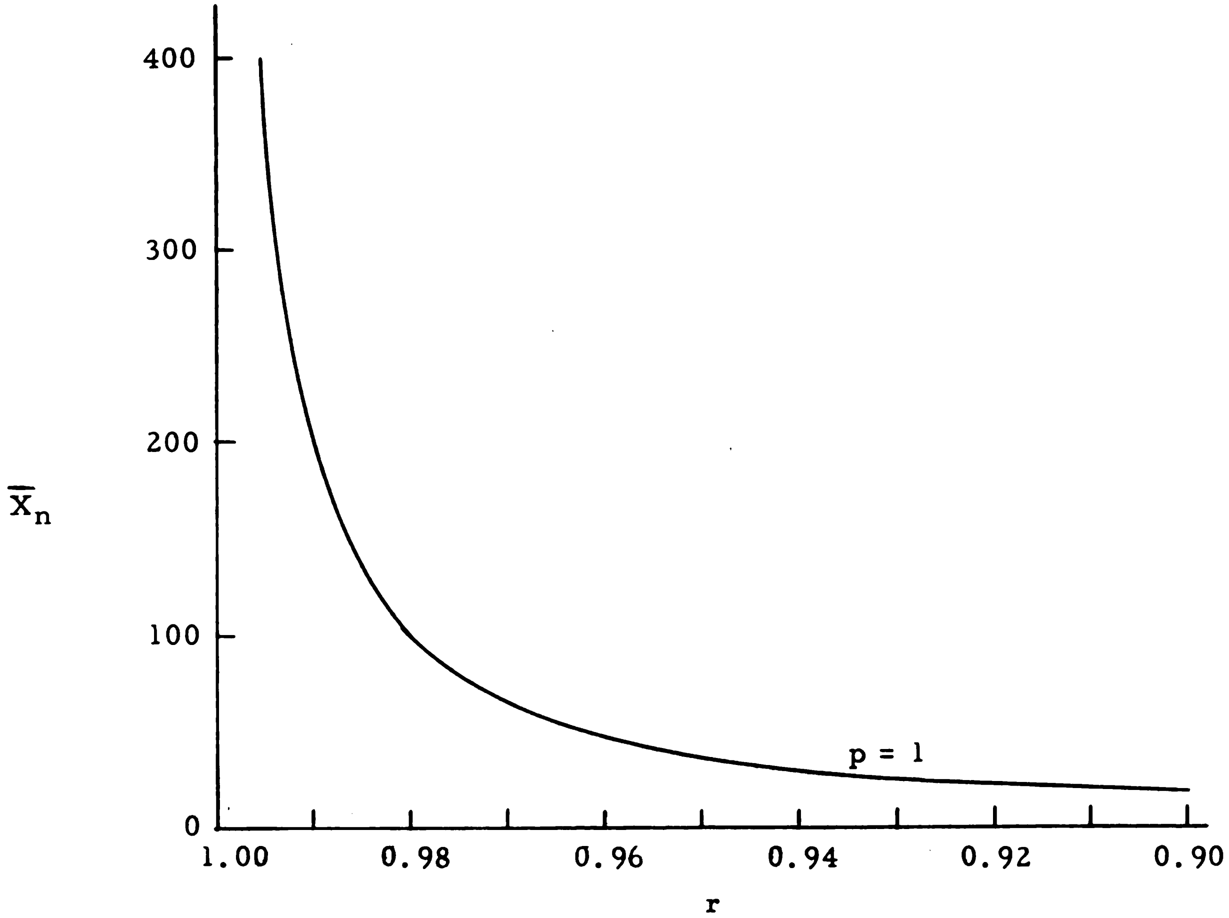


Figure 1. A plot of $\overline{X}_n$ vs. r calculated from equation 10.

condensation:

$$(CH_3)_3SiO^-: + (CH_3)_3Si\text{-}OCH_3 \rightleftarrows (CH_3)_3SiOSi(CH_3)_3 + CH_3O^-$$

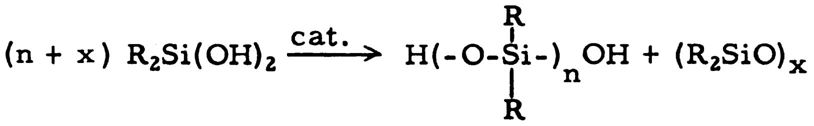
The silanolate ion concentration is proportional to the base catalyst concentration and was regarded as the active species.

It is presumed the above reactions would follow similar routes in aprotic solvents except that two molecules of silanol would now be involved in the condensation process (23);

$$\overset{H^+}{(CH_3)_3SiOH} + (CH_3)_3SiOH \rightleftarrows (CH_3)_3SiOSi(CH_3)_3 + H_3\overset{+}{O}$$

$$(CH_3)_3SiO^- + (CH_3)_3SiOH \rightleftarrows (CH_3)_3SiOSi(CH_3)_3 + OH^-$$

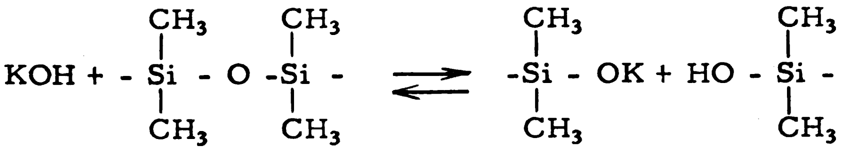
The mechanistic discussion up to this point has involved the condensation of monofunctional silanols. Although siloxane polymers can be formed in principle by the condensation of bifunctional silanols, such a reaction actually yields a mixture of low molecular weight polymers and cyclics:



$$(n + x)\ R_2Si(OH)_2 \xrightarrow{cat.} H(\text{-}O\text{-}\underset{R}{\overset{R}{Si}}\text{-})_nOH + (R_2SiO)_x$$

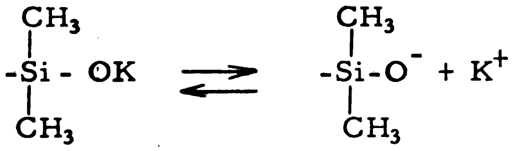
$$x = 3\text{-}8$$

High molecular weight siloxane polymers are generally prepared by catalytic opening and polymerization of cyclic siloxanes. Grubb and Osthoff have investigated this ring-opening process using octamethylcyclotetrasiloxane as the monomer and potassium hydroxide as the catalyst (24). Their results indicate a basic catalyst like potassium hydroxide reacts quantitatively with siloxane bonds to form potassium silanolate



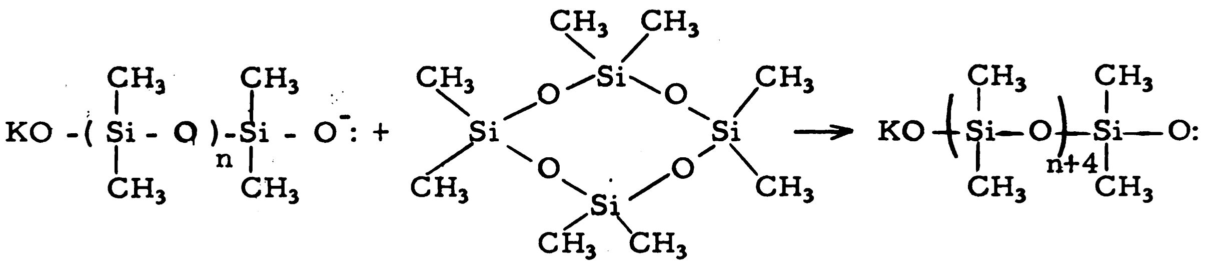
$$KOH + -\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}- \rightleftharpoons -\underset{CH_3}{\overset{CH_3}{Si}}-OK + HO-\underset{CH_3}{\overset{CH_3}{Si}}-$$

The silanolate partially ionizes to give silanolate anions



$$-\underset{CH_3}{\overset{CH_3}{Si}}-OK \rightleftharpoons -\underset{CH_3}{\overset{CH_3}{Si}}-O^- + K^+$$

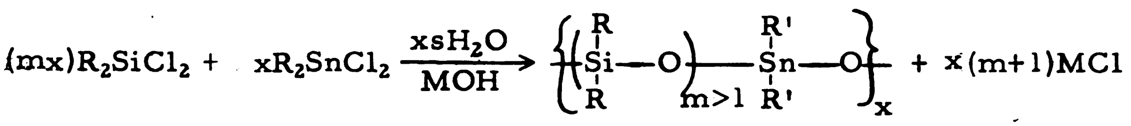
which act as the active species in the polymerization reaction. The propagation step of the reaction may be represented as



It is possible a similar catalytic polymerization of cyclic compounds could be employed to prepare high molecular weight metallosiloxane polymers (7).

D. Stannosiloxane Formation

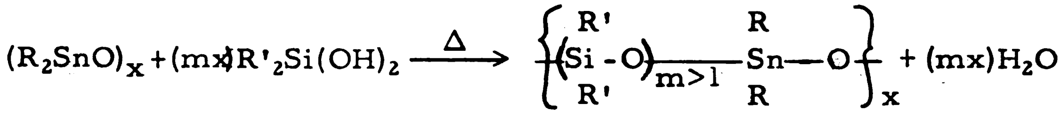
Syntheses of several stannosiloxane polymers have been reported (4, 11, 12, 13, 14). Andrianov first prepared such polymers by cohydrolysis of diorganodichlorosilanes and diorganotin dichlorides in the presence of excess base (12):



$$(mx)R_2SiCl_2 + xR_2SnCl_2 \xrightarrow[MOH]{xsH_2O} \left\{ \left(\underset{R}{\overset{R}{Si}}-O \right)_{m>1} - \underset{R'}{\overset{R'}{Sn}}-O \right\}_x + x(m+1)MCl$$

The initial hydrolysis products were transparent liquids soluble in organic solvents. They were transformed upon heating into insoluble, infusible solids. The polymers were not fully characterized. Koenig and co-workers repeated the original cohydrolysis process using dimethyltin dichloride and dimethyldichlorosilane as reactants (4,13). A rubbery plastic was isolated but not characterized except for silicon-tin analysis.

Koenig has also synthesized stannosiloxane polymers by the reaction of silanols with organotin oxides (13).



$$(R_2SnO)_x + (mx)R'_2Si(OH)_2 \xrightarrow{\Delta} \left\{ \left(\overset{R'}{\underset{R'}{Si}} - O \right)_{m>1} \overset{R}{\underset{R}{Sn}} - O \right\}_x + (mx)H_2O$$

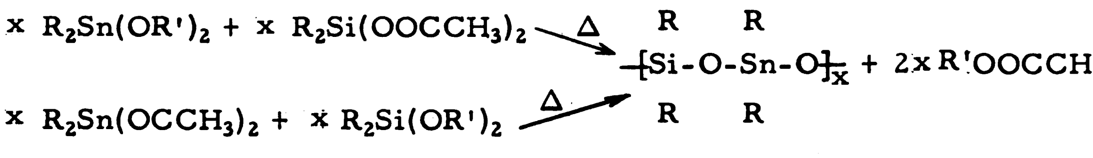
The products were for the most part brittle resins of low softening point (50-70°C). They were appreciably soluble in organic solvents and rapidly hydrolyzed by dilute mineral acids. $\overline{M}_n$ ranged from 1000 to 5000.

The cohydrolysis and silanol-organotin oxide reactions described above are not suited for the preparation of well-defined linear condensation polymers. They bring about a random integration of tin and silicon into a polymer chain and a $(Si\text{-}O\text{-}Sn\text{-}O)_x$ repeating chain is not obtained. For example, the cohydrolysis of trimethylchlorosilane with a dialkyltin dichloride yielded tetraalkyl-1, 3-bis-(trimethylsiloxy)-distannoxanes rather than bis(trimethylsiloxy)dialkylstannanes (25).

$$CH_3SiCl + R_2SnCl_2 \xrightarrow{xs\ NH_3} (CH_3)_3SiO(SnR_2O)_2Si(CH_3)_3$$

Because of this, the cohydrolysis and silanol-organotin oxide reactions were not considered suitable for the present study.

Two reactions which in principle can form stannosiloxane polymers with chains having an alternating Si-O-Sn-O structure are transesterification



$$x\ R_2Sn(OR')_2 + x\ R_2Si(OOCCH_3)_2 \xrightarrow{\Delta} -\!\!\left[\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Sn}}-O\right]_x + 2x\,R'OOCCH_3$$

$$x\ R_2Sn(OCCH_3)_2 + x\ R_2Si(OR')_2 \xrightarrow{\Delta} -\!\!\left[\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Sn}}-O\right]_x$$

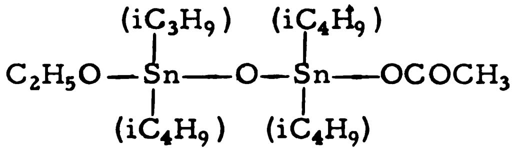
and the condensation of alkali metal silanolates with diorganotin dihalides.

$$y\ R_2Si(OM)_2 + yR_2SnX_2 \xrightarrow{\Delta} [Si\text{-}O\text{-}Sn\text{-}O\ ]_y + 2yMX$$

M = alkali metal.

O'Brien has prepared stannosiloxane polymers by the trans-esterification method (11). Waxy solids were obtained at reaction temperatures in excess of 200°C while viscous fluids were formed at lower temperatures. The polymers were not characterized beyond noting the physical appearance so it is not known whether or not copolymers with a 1:1 silicon-tin ratio were formed.

Henglein, Long, and Schmack obtained polymers by prolonged heating of dimethyldiethoxysilane with diisobutyldiacetoxytin at 120°C (26). From the low molecular weight products they isolated 1 ethoxy-3 acetoxy-tetraisobutyldistannoxane.



$$C_2H_5O\text{—}\underset{(iC_4H_9)}{\overset{(iC_3H_9)}{Sn}}\text{——}O\text{—}\underset{(iC_4H_9)}{\overset{(iC_4H_9)}{Sn}}\text{——}OCOCH_3$$

This clearly indicates side reactions do occur in the transesterification reaction under these conditions.

It is interesting to note that Okawara, <u>et</u> <u>al</u>. failed to obtain $(CH_3)_3SiOSn(CH_3)_3$ and compounds of the type $(CH_3)_3SiO\{Sn(CH_3)_2O\}_nSi(CH_3)_3$ by transesterification of trimethylethoxysilane with trimethyltin formate or dimethyltin diformate (25).

Koenig and Hutchinson reported the synthesis of stannosiloxane polymers by the condensation of $(NaO)_2Si\phi_2$ with ϕ_2SnCl_2 in dioxane (14). The $(NaO)_2Si\phi_2$ was prepared by reacting sodium metal with $(HO)_2Si\phi_2$ and used *in situ.* They refluxed the reaction mixture one hour and then let it stand several days at room temperature before isolating by filtration a precipitate which had formed. This precipitate was not pure sodium chloride, but otherwise was unidentified. A low molecular weight oily material was isolated from the dioxane filtrate. This contained

20.88% Sn and 7.16% Si. These values are not in good agreement with the theoretical values expected for a 1:1 silicon-tin copolymer (24.3% Sn and 5.76% Si). However, nothing was known about the $(NaO)_2Si\phi_2$ purity, so it is not surprising a 1:1 Si-Sn copolymer was not obtained.

Although both the transesterification and silanolate condensation reactions have been used to prepare low molecular weight stannosiloxane polymers, the nature of these reactions and the products obtained have not been thoroughly examined. A kinetic study of such reactions would be particularly difficult for the case of bifunctional systems since nothing is known about stannosiloxane chemistry. Only a few stannosiloxane compounds have been reported while no studies of the reactions involved in their formation have been made. Thus, it was concluded that the present study would deal principally with low molecular weight stannosiloxane compounds. The main purpose is to establish the stoichiometric and kinetic nature of reactions which can eventually be used in the formation of stannosiloxane polymers. The silanolate condensation reaction was selected since it has been established stannosiloxane compounds can be formed via this technique (16, 17).

Sommer, et al. appear to have been the first to use silanolates in organic syntheses. They prepared several organosiloxanes by the condensation of silanolates with organochlorosilanes (27). Gilman, Benedict, and Hartzfeld found this a generally useful method for preparing disiloxanes in high yields (28). Summers showed this reaction could be used to form a Si-O-metal linkage by condensing $NaOSi\phi_3$ with ϕ_3PbCl to give $\phi_3SiOPb\phi_3$ (29). The silanolate condensation reaction has since been used to prepare

$$\left\{(C_2H_5)_3SiO\right\}_3B(30),\quad \left\{(CH_3)_3SiO\right\}_4Ti(31),\quad \left\{(CH_3)_3SiO\right\}_3Sb(35).$$

Tatlock and Rochow (46) reported the synthesis of $\left\{(CH_3)_3SiO\right\}_2Sn$, $(CH_3)_3SiO\ {}_4Sn$, and $\left\{(CH_3)_3SiO\right\}_2Sn(CH_3)_2$, but did not characterize the product outside of recording the infrared spectra. Since this original synthesis, several investigators have prepared various other stannosiloxane compounds using the silanolate condensation reaction. Table III is a tabulation of known stannosiloxane compounds. Few analytical data have been reported for these and nothing is known about the reactions involved in their preparation.

Table III. Tabulation of Known Stannosiloxane Compounds.

Compound	m. p. (°C.)	b. p. (°C.)	Reference
$(CH_3)_3SiOSn(CH_3)_3$	-59	141	32
$[(CH_3)_3SiO]_2Sn(CH_3)_2$	48	160(decomp.)	16, 32
$[(CH_3)_3SiO]_3Sn(CH_3)$	34	155(decomp.)	32
$[(C_2H_5)_3SiO]_4Sn$	---	200-2/4 mm	33
$\phi_3SiOSn\phi_3$	138-139	--	17
$(\phi_3SiO)_2Sn(CH_3)_2$	166-167	--	13
	154-155	--	34
$(\phi_3SiO)_4Sn$	322(decomp.)	--	33

II. EXPERIMENTAL

A. Preparation of Reactants for Stannosiloxane Formation

1. Hexaphenyldisiloxane: $\phi_3\mathrm{SiOSi}\phi_3$ was prepared by the base catalyzed condensation of $\mathrm{HOSi}\phi_3$ in absolute ethanol. For example, a 30.0 g (0.109 mole) sample of $\mathrm{HOSi}\phi_3$ was refluxed with 0.28 g sodium hydroxide in 150 ml of absolute ethanol for 12 hours. The $\phi_3\mathrm{SiOSi}\phi_3$ precipitated during the reaction and after standing overnight at room temperature. The yield of crude product (m.p. 217-220°C) was 23.0 g (79.1%). After recrystallization from cyclohexane, the melting point increased to 224-225°C. All reported melting points are uncorrected and determined by the capillary method.

2. Sodium Triphenylsilanolate: $\mathrm{NaOSi}\phi_3$ was initially prepared by the reaction of $\mathrm{HOSi}\phi_3$ (Dow-Corning Purified Grade) with excess sodium metal in anhydrous ether (27). However, soluble products with neutralization equivalents corresponding to a purity greater than 95% could not be consistently obtained. A much more satisfactory method for $\mathrm{NaOSi}\phi_3$ preparation is due to Hyde, et al., which involves the cleavage of $\phi_3\mathrm{SiOSi}\phi_3$ with stoichiometric amounts of sodium hydroxide (36, 37),

$$\phi_3\mathrm{SiOSi}\phi_3 + 2\mathrm{NaOH} \rightleftharpoons 2\mathrm{NaOSi}\phi_3 + \mathrm{H_2O}$$

The equilibrium is forced to the right by removing the water formed from the reaction mixture.

In a typical preparation, 1.94 g. of sodium hydroxide (0.0485 mole) was pulverized in a dry box (38) and dissolved in 20 ml. of methanol. A stoichiometric amount of $\phi_3\mathrm{SiOSi}\phi_3$ (12.93 g., 0.0243 mole) was added to this solution together with 10 ml. of isopropanol. The slurry was heated to reflux temperature and 15 ml. of toluene added. Approximately

15 ml of solvent were slowly removed from the refluxing mixture via a Dean-Stark trap before 10 more ml of isopropanol were added to the reaction mixture. This concentration and addition procedure was repeated, usually two or three times, until a clear or slightly hazy solution was obtained. At this point, 5 ml isopropanol and 5 ml of toluene were added and approximately 15 ml of solvent once again removed. Finally 5 ml toluene were added and the now viscous solution concentrated another 5 or 7 ml. The reaction mixture was then cooled to room temperature. After overnight crystallization, the $\mathrm{NaOSi}\varnothing_3$ crystals were isolated by filtration and dried approximately 12 hours in vacuo at 50-55°C. The yield was 7.63 g (56.3%). The product was readily soluble in organic solvents. Its neutralization equivalent was determined by titration in absolute ethanol to a bromthymol blue end point. Calculated neutralization equivalent: 298.7. Found neutralization equivalent: 307.9, 308.0. All silanolates used in this study were 96 to 98% pure as determined by neutralization equivalents.

3. Sodium Diphenylsilanediolate. $(\mathrm{NaO})_2\mathrm{Si}\varnothing_2$ was prepared by a slight modification of Hyde's technique for synthesizing $\mathrm{NaOSi}\varnothing_3$ (36, 37). A 1.900 g (0.0475 mole) sample of powdered sodium hydroxide was dissolved in 20 ml of methanol. A stoichiometric amount of $(\mathrm{HO})_2\mathrm{Si}\varnothing_2$ (5.154 g, 0.0238 mole) and 10 ml of isopropanol were added to this solution. The slurry was raised to reflux temperature and 15 ml of toluene added. Thirty-three ml of solvent were then removed via a Dean-Stark trap over a three to four hour period before the clear reaction mixture was cooled to room temperature. After six hours, the $(\mathrm{NaO})_2\mathrm{Si}\varnothing_2$ crystals were removed by filtration and dried approximately 12 hours in vacuo at 65°C. The yield was 1.126 g (18.2%). Neutralization equivalents were determined in absolute ethanol as for $\mathrm{NaOSi}\varnothing_3$. Calculated neutralization equivalent: 260. Found neutralization equivalent: 265.8, 266.6.

Gibbs and co-workers (39), synthesized $(NaO)_2Si\phi_2$ by slowly adding an ether solution of $(HO)_2Si\phi_2$ to a sodium dispersion, and removing the insoluble product by filtration. No solvent could be found for the product. In contrast, the $(NaO)_2Si\phi_2$ prepared in this study was soluble in ethanol, but insoluble in benzene and toluene. It also dissolved in unpurified dimethylformamide, but was insoluble in dimethylformamide purified by the method of Thomas and Rochow (40).

4. Organotin Chlorides: All organotin chlorides were obtained from Metal and Thermit Corporation. Triphenyltin chloride $[\phi_3SnCl]$, diphenyltin dichloride $[\phi_2SnCl_2]$,and dimethyltin dichloride $[(CH_3)_2SnCl_2]$ were recrystallized from toluene at -14°C. Dibenzyltin dichloride $[(\phi CH_3)_2SnCl_2]$ was recrystallized from toluene at -4°C while dibutyltin dichloride $[(\underline{n}\text{-}C_4H_9)_2SnCl_2]$ was recrystallized from 30-60° petroleum ether at -4°C. Analytical data for all organotin chlorides used in this study are shown in Table IV.

B. Preparation of Stannosiloxane Compounds

A series of stannosiloxane compounds was prepared by dissolving $NaOSi\phi_3$ (0.006-0.010 mole) in 50 ml of benzene and adding to this solution a stoichiometric amount of the appropriate organotin chloride dissolved in 10-15 ml benzene. A slight increase in temperature was always observed indicating the condensation reaction is slightly exothermic. After mixing, the reaction mixture was allowed to stand five to fifteen minutes at room temperature before the sodium chloride precipitate was removed by filtration. The clear filtrate was taken to dryness *in vacuo* and the product recrystallized.

C. Solvent Purification

All solvents were distilled over calcium hydride through a 70 cm column packed with 5 mm glass helices. Thiophene-free benzene, the

Table IV. Organotin Chloride Analytical Data

		Analytical					
	m.p.	% Calculated			% Found		
Compound	(°C.)	C	H	Cl	C	H	Cl
ϕ_3SnCl	104.5-105.5	56.07	3.89	9.22	56.30	4.00	9.35
$(CH_3)_2SnCl_2$	106-108	10.92	2.73	32.32	10.87	2.71	32.57
$(\underline{n}\text{-}C_4H_9)_2SnCl_2$	41-42	31.61	5.93	23.38	31.79	6.12	23.13
ϕ_2SnCl_2	41.5-43.5	41.90	2.91	20.66	41.71	3.09	20.65
$(\phi CH_3)_2SnCl_2$		44.96	4.28	19.00	45.06	4.30	18.75

solvent for stannosiloxane formation, was fractionally crystallized before drying and distillation. The purified benzene, methanol, and isopropanol were stored in a desiccator when not in use. The measured refractive indices are compared with the literature values and shown in Table V.

D. Infrared Spectra

A Perkin-Elmer Model 21 spectrophotometer equipped with Connecticut Instrument cavity cells was used to obtain all infrared spectra recorded during this study. The spectra were recorded at concentrations below 2.0% (by weight). Such low concentrations were employed because of the intensity of the Si-O-Sn peak. Wright and Hunter have attributed this in the case of siloxanes to the ionic nature of the Si-O-Si bond (42).

E. Analytical

Carbon, hydrogen, and chlorine analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan, and Microtech Laboratories, Skokie, Illinois.

Combined oxides were determined by the method of Gilman and King (43). The stannosiloxane compound (0.3 to 0.4 g) was first treated with a four percent solution of bromine in carbon tetrachloride. The sample was then decomposed with a mixture of nitric, fuming nitric, and sulfuric acids before being ignited to give a white SiO_2 and SnO_2 residue. Silicon carbide formation was averted by igniting the decomposed sample slowly over a Bunsen burner and finally at 900°C in a muffle furnace. The average results shown in Table VI agree within ± 1.0% of the theoretical value.

Table V. Measured and Literature Refractive Indices for Solvents Used in the Study of Stannosiloxane Formation

Solvent	Measured n_D^{20}	Literature n_D^{20} (41)
Benzene	1.5008	1.5011
Toluene	1.4959	1.4969
Cyclohexane	1.4260	1.4262
Methanol	1.3289	1.3288
Isopropanol	1.3768	1.3776

Table VI. Stannosiloxane Combined Oxides

Sample	Sample Weight (g)	Theo. oxide Weight (g)	Found oxide Weight (g)	Recovery (%)
$\phi_3SiOSn\phi_3$	0.4084	0.1390	0.1377	101.1
	0.4020	0.1357	0.1357	100.0
	0.3705	0.1250	0.1247	99.7
	0.3652	0.1232	0.1241	100.8
			Av. =	100.4
$(CH_3)_2Sn(OSi\phi_3)_2$	0.3957	0.1531	0.1532	100.0
	0.4156	0.1610	0.1589	98.7
			Av. =	99.4
$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.3571	0.1235	0.1222	99.0
	0.3509	0.1214	0.1201	98.9
			Av. =	99.0
$\phi_2Sn(OSi\phi_3)_2$	0.3591	0.1180	0.1175	99.6
	0.3776	0.1243	0.1233	99.2
			Av. =	99.4
$(\phi CH_3)_2Sn(OSi\phi_3)_2$	0.3475	0.1103	0.1102	100.0
	0.3541	0.1124	0.1127	100.1
			Av. =	100.1

An attempt was made to carry out an independent tin analysis so that specific silicon and tin values could be reported. Samples were decomposed either by potassium iodate in sulfuric acid (12) or a mixture of fuming nitric and sulfuric acid (44). In both cases, the decomposed sample was reduced over lead (45) for 3 to 4 hours, cooled in an ice bath to approximately 4°C, and then titrated with standard iodine in a carbon dioxide atmosphere. Standard precautions were taken to exclude air from the reduced samples. Theoretical tin values were obtained for several standard organotin samples (Table VII). However, the stannosiloxanes gave erratic results which were consistently low as shown in Table VII. This pronounced variation is believed due to occlusion of small amounts of tin by the silica.

F. Stoichiometry

Figure 2 is a flow diagram of the procedure used to obtain stoichiometric and qualitative rate data for the formation of various stannosiloxane compounds in benzene. With this technique a closed material balance was established about a system containing semi-micro quantities of reactants.

In order to obtain sufficient material for analysis, 5 ml. aliquots (10 ml. for solutions below 0.02 N) of the reactant solutions were pipetted into the reactor, a 50 ml. Erlenmeyer flask. The solutions ranged in concentration from 0.007 to 0.05 N. After mixing, the reaction mixture was kept in the reactor for a known period at room temperature before being filtered into a tared 50 or 125 ml. filter flask. The clear filtrate was temporarily set aside.

All traces of benzene in the reactor and filter were removed by drying at 90°C. Upon cooling, the reactor was extracted with 10 ml. of distilled water. This solution was transferred to the filter and drawn into a clean 125 ml. filter flask. A second extraction with 5 ml. of water

Table VII. Tin Analytical Data

Sample	Decomposition Method	Theo. tin, (milliequivalents)	Found tin, (milliequivalents)	Recovery (%)
$(CH_3)_2SnCl_2$	HNO_3-H_2SO_4	1.351	1.374	100.2
ϕ_2SnCl_2	HNO_3-H_2SO_4	0.999	1.020	100.9
	HNO_3-H_2SO_4	1.063	1.074	101.0
$\phi_3SiOSn\phi_3$	HNO_3-H_2SO_4	1.280	1.171	91.5
	HNO_3-H_2SO_4	1.360	1.324	97.4
	HNO_3-H_2SO_4	0.956	0.933	97.6
	KIO_3	1.042	1.027	98.5
	KIO_3	1.220	1.183	97.0
	KIO_3	1.289	1.213	94.1
$(\underline{n}$-$C_4H_9)_2Sn(OSi\phi_3)_2$	HNO_3-H_2SO_4	0.891	0.868	97.4
	KIO_3	0.928	0.864	93.0
$(\phi CH_3)_2Sn(OSi\phi_3)_2$	KIO_3	0.840	0.835	99.4

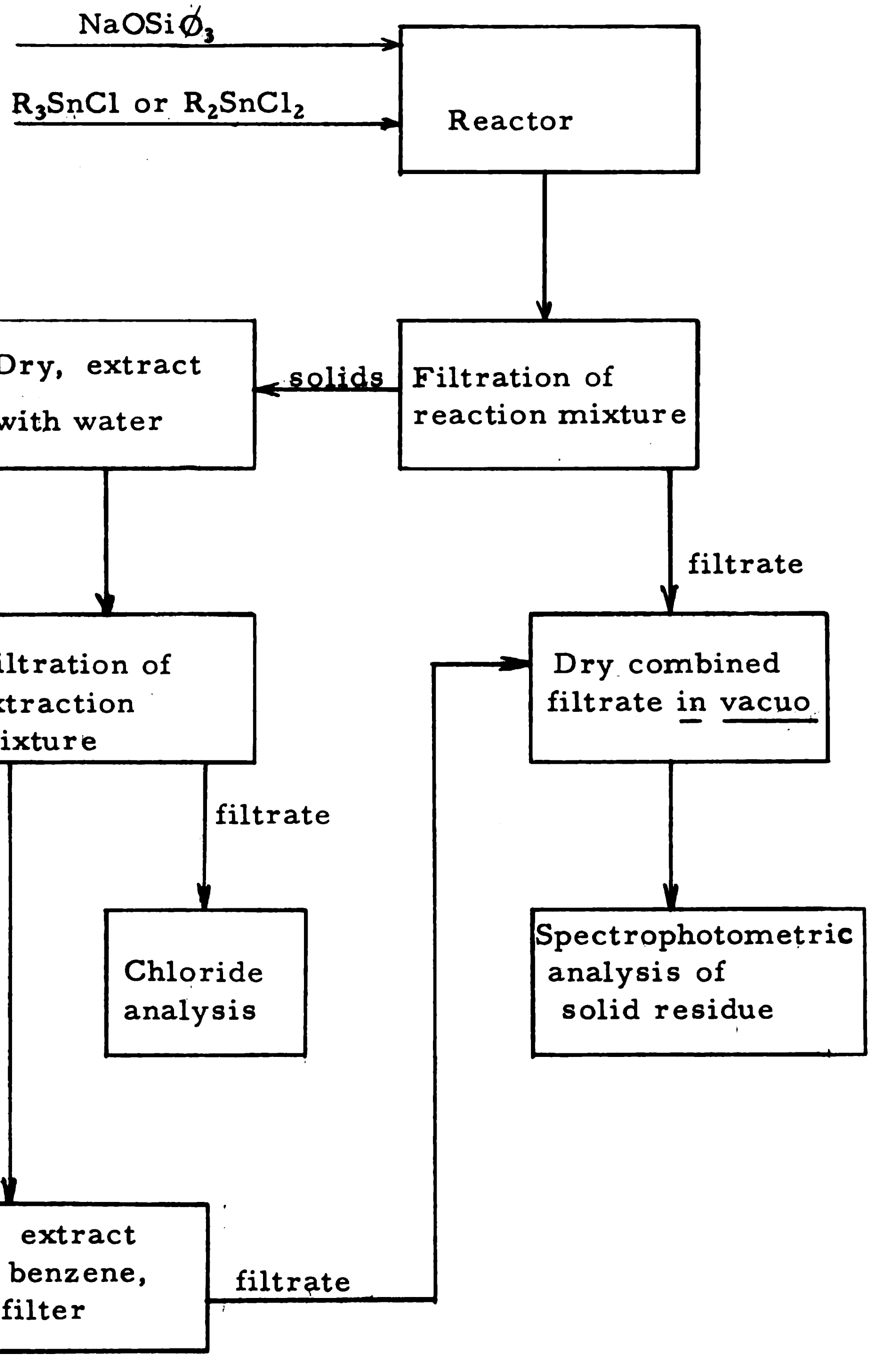


Figure 2. Flow diagram of stoichiometry procedure.

was used to insure complete removal of sodium chloride from the reactor and filter. Chloride present in the combined water extract (15 ml.) was determined by titration with 0.0200 N standard silver nitrate using dichlorofluorescein as the indicator.

Several standard chloride analyses were carried out to establish the effectiveness of the above extraction and titration method. Known amounts of reagent grade sodium chloride were pulverized, dried at 105°C, and suspended in the reactor with 10 ml. aliquots of benzene solutions containing $\phi_3SiOSn\phi_3$ or various organotin chlorides. The results in Table VIII indicate that in the presence of $\phi_3SiOSn\phi_3$ the average recovery is 99.0% with a standard deviation (σ) of $\pm$ 0.2%. The presence of organotin chlorides did not appear to significantly affect chloride recovery except in the case of $(CH_3)_2SnCl_2$ where the effect is small.

After the water extraction, the reactor and filter were dried at 105°C. Upon cooling, the reactor was extracted with 10 ml. benzene. The extract was transferred to the filter and drawn into the tared 125 ml filter flask containing the original benzene filtrate. A second 10 ml. benzene extraction was used to assure complete removal of solids from the walls of the reactor and filter. The combined benzene filtrate was taken to constant weight *in vacuo* and the weight of the solid residue determined by difference. The amount of stannosiloxane compound present in this residue was measured spectrophotometrically using the characteristic Si-O-Sn peak for identification. Reaction conditions and material balance data obtained in this manner are tabulated in Appendix A.

Beer's Law is expressed as

$$A_\lambda = \sum_{\underline{i}} \epsilon_{\underline{i}\lambda} bc_{\underline{i}} \qquad (12)$$

A_λ = absorbancy at wavelength λ; b = cell path length, cm;

$c_{\underline{i}}$ = concentration of $\underline{i}^{th}$ component in solution, $\underline{M}$;

$\epsilon_{\underline{i}\lambda}$ = molar absorptivity of $\underline{i}^{th}$ component at λ, (1/$\underline{M}$ cm).

Table VIII. Standard Chloride Analyses

Suspension Medium*	Theo. Sodium chloride (milliequivalents)	Recovered Sodium chloride (milliequivalents)	Recovery (%)
0.0169 $\underline{\mathrm{M}}$ $\phi_3\mathrm{SiOSn}\phi_3$	0.2649	0.2628	99.2
	0.2495	0.2474	99.1
	0.1880	0.1864	99.2
	0.2513	0.2464	98.1
	0.2444	0.2438	99.8
	0.2821	0.2802	99.3
	0.2325	0.2272	97.7
	0.2154	0.2134	99.1
	0.2444	0.2422	99.1
		Average:	99.0,
		σ = ± 0.2%	
0.0127 $\underline{\mathrm{M}}$ $(\underline{n}\text{-}C_4H_9)_2SnCl_2$	0.2239	0.2230	99.6
	0.2701	0.2666	98.7
0.0127 $\underline{\mathrm{M}}$ $(CH_3)_2SnCl_2$	0.3522	0.3544	100.6
	0.2735	0.2786	101.9
0.0254 $\underline{\mathrm{M}}$ $\phi_3\mathrm{SnCl}$	0.2034	0.2030	99.8

*Ten ml. of solution used for each run.

Examination of infrared spectra of the reactants and products established that only the intense Si-O-Sn peak in the various stannosiloxane compounds absorbed significantly in the 10.3 to 10.6 μ region. $NaOSi\phi_3$ has a strong narrow peak at 10.25 μ, but this falls off sharply so that by 10.40 μ it contributes negligible absorption over the concentration range employed in this study. Hence, all $\epsilon_{\underline{i}\lambda}$'s in this region except that for the Si-O-Sn peak are essentially zero and equation 12 may be rewritten for a given stannosiloxane compound as:

$$A = \epsilon bc \tag{13}$$

A = absorbancy of Si-O-Sn peak; b = cell path length, cm; c = concentration of stannosiloxane compound, $\underline{M}$; ε = molar absorptivity of Si-O-Sn peak, $1/\underline{M}$ cm.

In order to carry out spectrophotometric determinations of various stannosiloxanes, it was first necessary to prepare calibration plots for each compound studied. Solutions of known concentrations ranging from 0.0055 to 0.0091 $\underline{M}$ were prepared using purified $\phi_3SiOSn\phi_3$, $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, and $(CH_3)_2Sn(OSi\phi_3)_2$ samples. Cyclohexane was used as the solvent for $\phi_3SiOSn\phi_3$ and $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, while carbon disulfide was employed for $(CH_3)_2Sn(OSi\phi_3)_2$. The infrared spectra for each solution were recorded on 10 x 10 cm chart paper. The operating procedure followed the Perkin-Elmer Instruction Manual (46). Scatter of the data due to solvent evaporation from the cells was minimized by scanning only the region from 8.5 to 11.0 μ. Eight and one-half μ was selected as the 100% transmission reference point because the the stannosiloxanes have relatively little absorption at this point over the concentration range used.

The calibration plots for $\phi_3SiOSn\phi_3$, $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, and $(CH_3)_2Sn(OSi\phi_3)_2$ are shown in Figures 3, 4, and 5. In all cases, Beer's Law was obeyed over the concentration range investigated. The method of least squares was used to draw the best straight line through the experimental points.

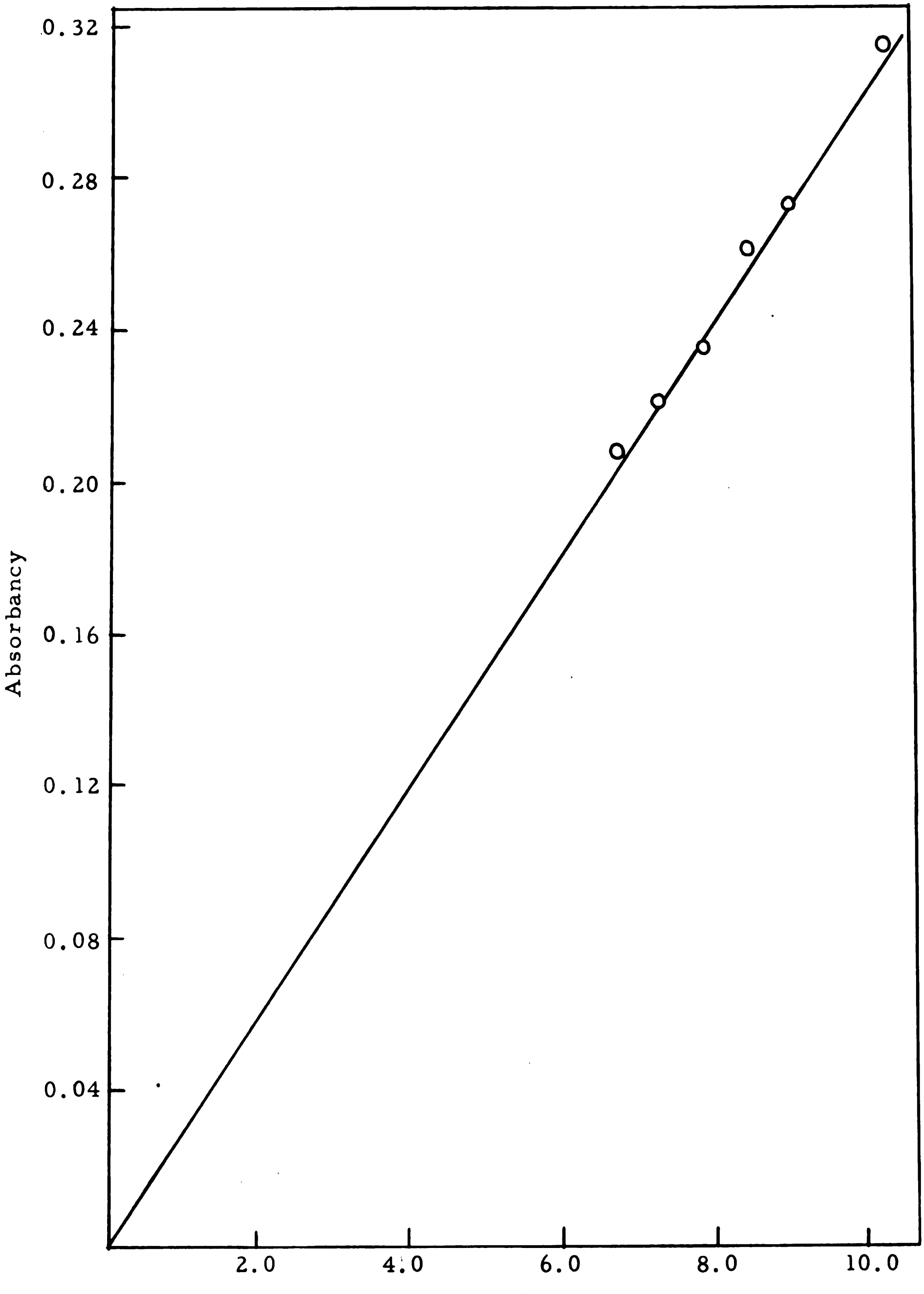


Figure 3. $\phi_3SiOSn\phi_3$ Beer's Law Calibration Plot, C_6H_{12} = Solvent.

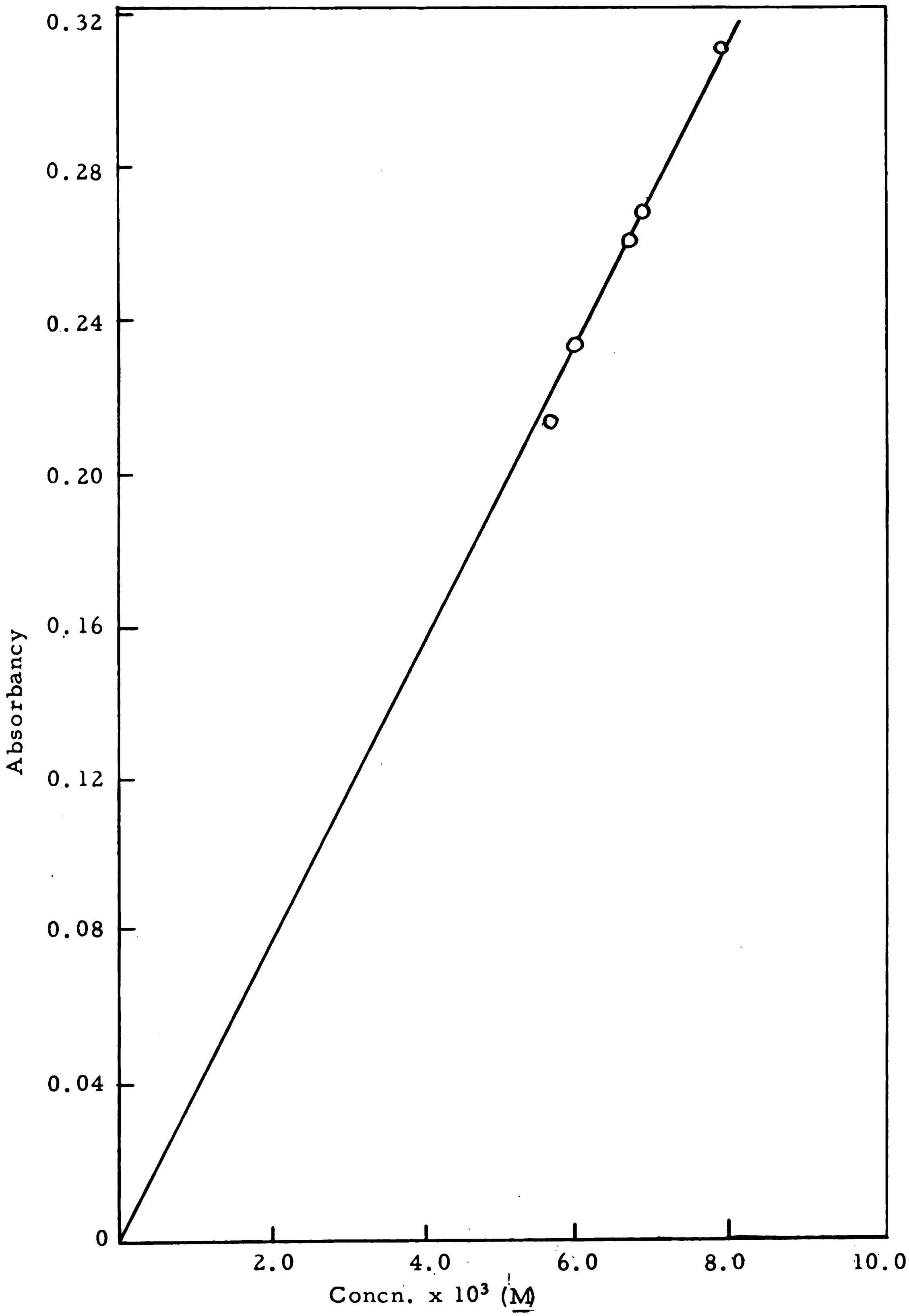


Figure 4. $(CH_3)_2Sn(OSi\Phi_3)_2$ Beer's Law Calibration Plot, CS_2 = Solvent.

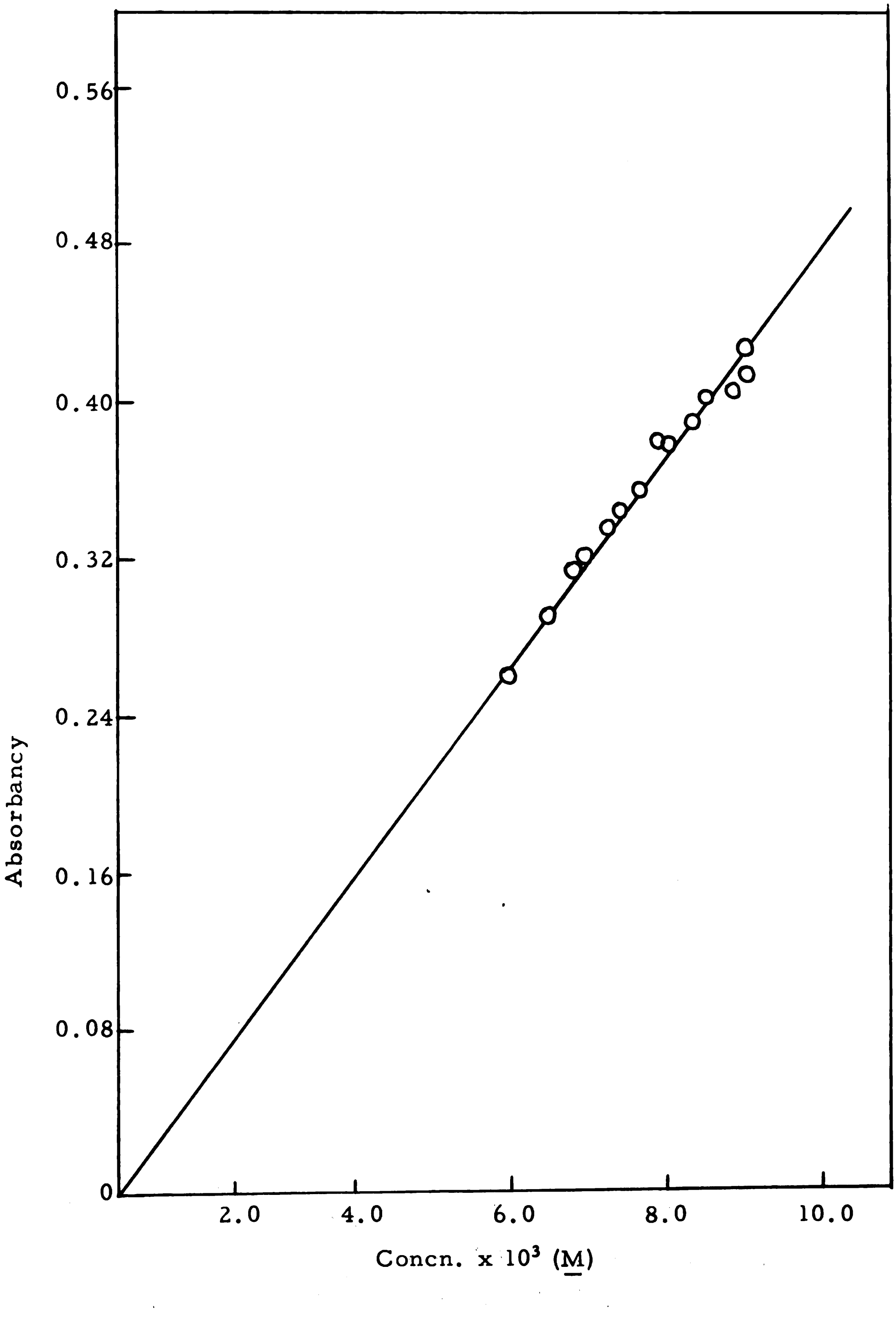


Figure 5. $(\underline{n}C_4H_9)_2Sn(OSi\phi_3)_2$ Beer's Law Calibration Plot, $\underline{C}_6H_{12}$ = Solvent.

The yield of a stannosiloxane compound in a given reaction mixture was determined by preparing a solution (cyclohexane or carbon disulfide) of the solid residue with a known concentration (c_0, M). Absorbancy of the Si-O-Sn peak was then measured as outlined above and the concentration (c, M) of the stannosiloxane compound actually present in the solution taken from the appropriate Beer's Law calibration plot. The yield (%) was calculated from the relation

$$Y = (c/c_0) \times 10^2 \tag{14}$$

A, c_0, c, and Y values for each of the reaction mixtures investigated are reported in Appendix B.

When equation 14 is used, it is assumed that complete material balance closure had been achieved in the above stoichiometric procedure. Representative data from Appendix A (Table IX) show the average closure is 99.8%, $\sigma = \pm 1.4\%$, and hence, the assumption is justified.

A measure of the error inherent in the spectrophotometric analysis of stannosiloxane compounds is given by the scatter of the data about the least squares Beer's Law line. Table X shows that a deviation from this line of up to ± 3.7% can occur for a given c/c_0 value. However, most errors fall within ± 2.0%. Much of this scatter is due to instrumental errors as shown by the duplicate $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ determinations obtained for several reaction mixtures (Table XI).

G. Polymer Formation

Several stannosiloxane polymers were synthesized by the in situ condensation of $(NaO)_2Si\phi_2$ with $(\underline{n}\text{-}C_4H_9)_2SnCl_2$. Specific reaction conditions and material balances for each experiment are presented in Table XII. The reaction procedure followed is outlined below.

In order to carry out a polymerization reaction, $(NaO)_2Si\phi_2$ was prepared in a 100 ml round bottom reactor by dissolving 0.04 to 0.05

Table IX. Representative Material Balance Data

Organotin Chloride	Reactant Concn. (M)	Sodium Chloride Recovered (g)	Solid Residue Recovered (g)	Theoretical Solids (g)	Recovery (%)
$(CH_3)_2SnCl_2$	0.04895	0.0272	0.1711	0.1997	99.30
	0.04895	0.0273	0.1734	0.1997	100.50
	0.04895	0.0271	0.1711	0.1997	99.25
ϕ_3SnCl	0.0127	0.0143	0.1578	0.1736	99.14
	0.0127	0.0148	0.1595	0.1736	100.40
	0.0127	0.0146	0.1571	0.1736	98.91
	0.04895	0.0272	0.2991	0.3343	97.60
	0.04895	0.0271	0.29960	0.3343	97.73
$(\underline{n}\text{-}C_4H_9)_2SnCl_2$	0.026	0.0147	0.1033	0.1170	100.85
	0.026	0.0146	0.1019	0.1170	99.57
	0.026	0.0147	0.1016	0.1170	99.40
	0.04895	0.0271	0.1924	0.2202	99.68
	0.04895	0.0270	0.1971	0.2202	101.77
	0.04895	0.0272	0.1991	0.2202	102.77
				Average	99.8%,
					$\sigma = \pm 1.4\%$

Table X. Scatter of Data Used to Plot Beer's Law Calibration Curves

Run	c_0(M)	c(M)		$c/c_0 \times 10^2$
($\underline{n}$-C_4H_9)$_2$Sn(OSiϕ_3)$_2$	0.00756	0.00758		100.3
	0.00506	0.00491		97.0
	0.00556	0.00554		99.6
	0.00587	0.00598		101.9
	0.00600	0.00608		101.3
	0.00631	0.00635		100.6
	0.00646	0.00651		100.8
	0.00690	0.00717		103.9
	0.00705	0.00716		101.6
	0.00756	0.00755		99.9
	0.00790	0.00763		96.6
	0.00805	0.00782		97.1
	0.00671	0.00669		99.7
	0.00738	0.00738		100.0
	0.00802	0.00802		100.0
			range	103.9 to 96.6%
ϕ_3SiOSnϕ_3	0.01012	0.01022		101.0
	0.00784	0.00767		97.8
	0.00893	0.00887		99.3
	0.00719	0.00720		100.1
	0.00836	0.00849		101.6
			range	101.6 to 97.8%
(CH_3)$_2$Sn(OSiϕ_3)$_2$	0.00790	0.00797		100.9
	0.00687	0.00687		100.0
	0.00667	0.00670		100.4
	0.00598	0.00690		100.3
	0.00501	0.00548		97.7
			range	100.9 to 97.7%

Table XI. Duplicate $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ Determinations

Run	$c_0(\underline{M})$	A	$c(\underline{M})$	$c/c_0 \times 10^2$
21	0.00662	0.339	0.00641	96.8
	0.00662	0.326	0.00617	93.2
22	0.00811	0.404	0.00762	94.0
	0.00811	0.409	0.00771	95.1
24	0.00664	0.312	0.00590	88.9
	0.00664	0.311	0.00589	88.7
26	0.00636	0.305	0.00578	90.9
	0.00636	0.309	0.00584	91.8
29	0.00659	0.352	0.00666	101.1
	0.00659	0.355	0.00670	101.7
30	0.00613	0.321	0.00608	99.2
	0.00613	0.325	0.00615	100.3
38	0.00770	0.319	0.00610	79.2
	0.00770	0.317	0.00590	76.6
39	0.00698	0.263	0.00497	71.2
	0.00698	0.275	0.00519	74.4
40	0.00809	0.387	0.00730	90.2
	0.00809	0.390	0.00736	91.0

Table XII. Material Balance Data for *In Situ* Preparation of Stannosiloxane Polymers

Sample	($\underline{n}$-C_4H_9)$_2$$SnCl_2$ added (mole)	Reaction time (min.)	Reaction temperature(°C)	Sodium Chloride recovery (%)	Total bulk polymer recovered (%)
ϕ-Bu I	0.0250	108	-4	98.0	99.2
ϕ-Bu II	0.0226	30	reflux	97.4	98.2
ϕ-Bu III	0.0249	3042	-14	97.7	---
ϕ-Bu IV	0.0206	1440	reflux	97.1	87.4

mole of powdered sodium hydroxide in 20 ml of methanol. A stoichiometric amount of $(HO)_2Si\phi_2$ and 10 ml of isopropanol were added and the slurry raised to reflux temperature. At this point 15 ml of toluene were added. Twenty ml of solvent were then removed from the refluxing reaction mixture via a Dean-Stark trap over a two hour period. The clear silanolate solution was finally brought to the desired polymerization temperature and a stoichiometric amount of $(\underline{n}\text{-}C_4H_9)_2SnCl_2$, dissolved in 18 ml of toluene and 8 ml of isopropanol, added. It was assumed that a 100% $(NaO)_2Si\phi_2$ yield had been obtained. After the reaction, the products were filtered into a tared filter flask and the clear filtrate was temporarily set aside.

The reactor and filter were dried at 110°C before the former was extracted with 25 ml of water. This solution was transferred to the filter and drawn into a clean 125 ml filter flask. A second 25 ml water extraction was made before the reactor and filter were dried at 110° C and then extracted twice with 25 ml aliquots of hot toluene.

After drying at 110°C, a third extraction with 25 ml of water was made. The combined water extracts were transferred quantitatively to a 100 (or 250) ml volumetric flask and diluted to proper volume. Three five-ml aliquots were pipetted from the volumetric and each titrated with 0.1 N standard silver nitrate using dichlorofluorescein as the indicator. Total chloride recovery was calculated from the average of these runs. The 3 runs deviated from this mean by $< \pm 0.5\%$. The clear filtrates were combined and taken to constant weight *in vacuo* in order to determine the yield of bulk polymer. A small amount of solid material (~1-2% of total solids) insoluble in hot toluene was discarded.

Polymers ϕ-Bu II and ϕ-Bu III were prepared exactly by the technique outlined above. A slight modification was made for polymer ϕ-Bu IV. After the original reaction mixture was filtered, the clear filtrate was concentrated to half its original volume and allowed to stand overnight. The precipitate which formed was removed by filtration and the clear filtrate taken to dryness in vacuo. Thus, the ϕ-Bu IV bulk polymer was divided into two fractions. In the case of polymer ϕ-Bu I the $(NaO)_2Si\phi_2$ preparation was modified by adding 10 ml of benzene along with the 15 ml. of toluene. Approximately 30 ml. of solvent were slowly removed from the refluxing reaction mixture via the Dean-Stark trap before 10 ml. of isopropanol were added. Another 15 ml. of solvent were removed and 5 ml. of toluene added. The $(n\text{-}C_4H_9)_2SnCl_2$ was then added and the previously outlined procedure was followed.

H. Polymer Fractionation

Polymers prepared by the in situ condensation of $(NaO)_2Si\phi_2$ with $(n\text{-}C_4H_9)_2SnCl_2$ were extracted with methanol and thereby separated into a resilient solid and a viscous liquid fraction. The room temperature fractionation was carried out by extracting 4.1 to 6.9 g of polymer with 25 ml of methanol in a 125 ml Erlenmeyer. Large clumps of the bulk polymer were broken up and the extraction mixture agitated occasionally. After 48 hours, a fine solid material was removed by filtration. The clear filtrate and the solid fraction retained on the filter were dried to constant weight in vacuo. Material balances for each of the fractionation experiments are shown in Table XIII.

I. Solubility Studies

Solubility characteristics of the bulk and fractionated stannosiloxane polymers were determined in a number of solvents at room temperature. A 0.01 ± 0.001 g. polymer sample was placed in a 10 x 75 mm. test tube together with one ml. of solvent. After standing several days with occasional agitation, the sample was examined and classified as soluble (clear solution), partly soluble (> 50% soluble), slightly soluble (< 50% soluble), and insoluble (no visible dissolution). Results are shown in Appendix C.

Table XIII. Material Balance Data for Stannosiloxane Polymer Fractionations

Sample	Bulk polymer sample (g)	Methanol-insoluble fraction (%)	Methanol-soluble fraction (%)
ϕ-Bu I	4.10	78.5	21.5
ϕ-Bu II	5.72	71.5	28.5
ϕ-Bu III	6.89	54.6	45.4

None of the bulk polymers or methanol-insoluble fractions were soluble at room temperature in the solvents investigated. However, all formed clear solutions in hot (110°C) n-amyl acetate and no precipitation occurred upon cooling to room temperature. The methanol-soluble fractions readily dissolved in every solvent investigated except isopropanol and acetonitrile.

The bulk stannosiloxane polymers have peculiar solubility characteristics. The polymers were soluble in the original reaction mixture, but after being dried, they were not soluble in a wide variety of solvents at room temperature. The resilient solids isolated by methanol extraction of the bulk polymers were insoluble at room temperature in all solvents examined. This insolubility may be due to crystallization.

III. RESULTS AND DISCUSSION

A. Stannosiloxane Synthesis and Characterization

A series of stannosiloxane compounds has been synthesized by the procedure outlined in the experimental section of this dissertation. Pertinent data are listed in Table XIV. Only carbon-hydrogen analyses are reported here; combined Si-Sn oxides have been reported in Table VI. All of the compounds are white, crystalline solids with low to moderate melting points. Their solubility characteristics vary considerably. $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ is very soluble in most organic solvents at room temperature. $\phi_3SiOSn\phi_3$, $(CH_3)_2Sn(OSi\phi_3)_2$, and $(\phi CH_3)_2Sn(OSi\phi_3)_2$ are only moderately soluble at room temperature, but dissolve readily when heated. $\phi_2Sn(OSi\phi_3)_2$ is relatively insoluble in most solvents even when heated, but does dissolve in hot o-xylene. All of these compounds are sparsely soluble in alcohols. Because of their solubility characteristics, the stannosiloxanes were relatively easy to purify. Diethyl ether (-4°C) was used for recrystallization of $\phi_3SiOSn\phi_3$ while o-xylene (-14°C) was employed for $\phi_2Sn(OSi\phi_3)_2$. $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, $(CH_3)_2Sn(OSi\phi_3)_2$ and $(\phi CH_3)_2Sn(OSi\phi_3)_2$ were recrystallized from n-heptane (-4°C). No attempt was made to increase the reported yields by successive concentrations and crystallizations of the mother liquors.

The compounds, $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ and $(\phi CH_3)_2Sn(OSi\phi_3)_2$, are new and have not been reported previously. The $\phi_3SiOSn\phi_3$ prepared in this investigation appears to be the same material reported by Post and Papetti (17). Likewise, the $(CH_3)_2Sn(OSi\phi_3)_2$ reported in the present study appears to be similar to the material obtained by Chamberland from the same reaction (34). Chamberland gave no analytical data, but reported only the melting point. Koenig (4) claimed to have prepared

Table XIV. Stannosiloxane Compounds Prepared by Silanolate Condensation Reaction In Benzene

Compound	Moles of $NaOSi\phi_3$ used	m.p. (^{o}C)	Yield (%)	Analytical Calculated C(%)	Analytical Calculated H(%)	Analytical Found C(%)	Analytical Found H(%)
$\phi_3SiOSn\phi_3$	0.00612	139-140	59.7	69.15	4.80	69.33	4.84
$(CH_3)_2Sn(OSi\phi_3)_2$	0.00708	155-156	64.9	65.26	6.01	65.44	5.92
$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.00677	69-70	79.5	67.46	6.90	67.61	6.57
$\phi_2Sn(OSi\phi_3)_2$	0.00758	148.5-149.5	40.2	70.01	5.83	70.05	5.64
$(\phi CH_3)_2Sn(OSi\phi_3)_2$	0.00958	122-123	78.3	70.36	5.39	70.41	5.31

$(CH_3)_2Sn(OSi\phi_3)_2$ (m.p. 165-166°C) by cohydrolysis of $HOSi\phi_3$ with dimethyltin oxide, but no carbon-hydrogen analyses were reported and his Si-Sn data differ from the theoretical value by 3-4%. The Si-Sn analytical procedure was not described. Koenig and Crain (13) attempted to prepare $\phi_2Sn(OSi\phi_3)_2$ by cohydrolysis of $HOSi\phi_3$ with $(\phi_2SnO)_x$, but a product corresponding to $Sn(OSi\phi_3)_4$ was isolated. Thus, it appears the cohydrolysis procedure is not a satisfactory method for preparing well-defined stannosiloxane compounds. In contrast, such compounds have been obtained in good yield by the condensation of $NaOSi\phi_3$ with various organotin chlorides. This synthesis is rapid, easy to carry out, and employs mild reaction conditions so that side reactions which might become significant at elevated temperatures are minimized. These factors made the silanolate condensation reaction ideally suited to the synthesis of well-defined stannosiloxane compounds.

Infrared spectra for the stannosiloxane compounds prepared in this study are shown in Appendix D while characteristic peaks are listed in Table XV. As in the case of organosiloxanes (42, 47, 48), the most interesting feature of these spectra is the great intensity of the bands lying in the 8 to 14 μ region. The intensity may be due at least in part to the partial ionic character of the Si-O-Sn, Si-R, and Sn-R bonds. This explanation is analogous to that offered by Wright and Hunter for the organosiloxanes (42).

Stannosiloxane compounds are readily identified by a broad and intense absorption peak in the 10.3 to 10.7 μ region which is attributed to the Si-O-Sn bond. This peak lies at 10.3-10.4 μ in $\phi_3SiOSn\phi_3$, but is shifted to approximately 10.7 μ in $(CH_3)_2Sn(OSi\phi_3)_2$, $\phi_2Sn(OSi\phi_3)_2$, and $(\phi CH_3)_2Sn(OSi\phi_3)_2$. It lies at 10.6 μ in $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$. Other identifying peaks used in this study are those lying at 9.0, 9.7, 13.5-13.6, and 14.2 μ. These are bands characteristic of phenyl on silicon (47). The peak lying at 13.8 μ in $\phi_3SiOSn\phi_3$ and $\phi_2Sn(OSi\phi_3)_2$ is probably due to the ϕ-Sn linkage.

Table XV. Infrared Absorption Peaks of Stannosiloxanes in Carbon Disulfide

Compound	Peak Location, μ
ϕ_3SiOSnϕ_3	3.3(w)*, 9.0(s), 9.3(w), 9.7(w), 10.0(m), 10.3-10.4(s), 13.5(m), 13.8(s) 14.2(s), 14.4(s)
$(CH_3)_2Sn(OSi\phi_3)_2$	3.3(w), 9.1(s), 10.7(s), 13.1(m), 13.6(m), 14.4(s)
$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	3.3(w), 3.5(w), 9.0)s), 9.7(w), 10.6(s), 13.5(m), 14.2-14.4(s)
$\phi_2Sn(OSi\phi_3)_2$	3.3(w), 9.0)s), 9.7(w), 10.7(s), 13.6(m), 13.8(s), 14.4(s)
$(\phi CH_3)_2Sn(OSi\phi_3)_2$	3.3(w), 9.0(s), 9.7(w), 10.7(s), 13.3(m), 13.5(m), 14.2(s), 14.4(s)

*Peak Intensities: (w) = weak; (m) = medium; (s) = strong.

Relatively little is known about the general stability of stannosiloxane compounds. Schmidtbauer and Schmidt have reported $(CH_3)_3SiOSn(CH_3)_3$ was hydrolytically unstable (32) while Koenig (4) found stannosiloxanes were readily cleaved by dilute mineral acids. Although no specific attempt was made to examine stability in the present study, it was possible to show $\phi_3SiOSn\phi_3$, $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, and $(CH_3)_2Sn(OSi\phi_3)_2$ are not highly labile. Several stoichiometric runs involving these compounds were allowed to stand for extended periods at room temperature before the reaction products were isolated and characterized. The yields from these runs (Table XVI) are essentially quantitative. There is no evidence the stannosiloxane compounds are unstable under the reaction conditions employed in this investigation. The high yields of purified products obtained by recrystallizations from hot n-heptane and o-xylene are further evidence the stannosiloxanes are stable compounds under mild conditions.

B. Stoichiometry and Rate of Stannosiloxane Formation

Stoichiometric results for the reaction of $NaOSi\phi_3$ with ϕ_3SnCl in benzene are listed in Table XVII. Similar data for the reaction of $NaOSi\phi_3$ with $(\underline{n}\text{-}C_4H_9)_2SnCl_2$ and $(CH_3)_2SnCl_2$ in benzene are shown in Tables XVIII and XIX. Two to five runs were usually made at each initial reactant concentration. Equivalent proportions of reactants were always used. The reactions were carried out at room temperature.

The $\phi_3SiOSn\phi_3$, $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, and $(CH_3)_2Sn(OSi\phi_3)_2$ yields are consistent with the over-all equations:

$$NaOSi\phi_3 + \phi_3SnCl \longrightarrow \phi_3SiOSn\phi_3 + NaCl$$

$$2NaOSi\phi_3 + (\underline{n}\text{-}C_4H_9)_2SnCl_2 \longrightarrow (\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2 + 2NaCl$$

$$2NaOSi\phi_3 + (CH_3)_2SnCl_2 \longrightarrow (CH_3)_2Sn(OSi\phi_3)_2 + 2NaCl$$

Table XVI. Stannosiloxane Stability in Benzene at Room Temperature

Run Number	Initial $NaOSi\phi_3$ Concentration, (N)	Reaction time (min.)	Stannosiloxane yield (%)
$\phi_3SiOSn\phi_3$			
7	0.0127	2796	103.2
10	0.0134	1447	97.2
18	0.0345	2994	98.5
20	0.0490	2225	96.3
$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$			
23	0.0127	2978	96.6
26	0.0134	8878	91.4
30	0.0147	1207	99.8
33	0.0260	2153	93.7
$(CH_3)_2Sn(OSi\phi_3)_2$			
59	0.0127	2887	88.5
62	0.0134	8811	82.7
69	0.0260	2795	96.4
78	0.0490	2190	97.0

Table XVII. $\phi_3SiOSn\phi_3$ Stoichiometric Results

Run Number	Initial $NaOSi\phi_3$ and ϕ_3SnCl concns. (N)	Sodium chloride yield (%)	$\phi_3SiOSn\phi_3$ yield (%)
1	0.00783	95.3	97.5
2	0.00783	95.9	98.7
3	0.00783	95.1	96.3
4	0.00783	96.3	99.1
5	0.0127	96.2	96.7
6	0.0127	99.6	100.2
7	0.0127	98.0	103.2
8	0.0134	93.4	93.6
9	0.0134	94.3	99.3
10	0.0134	94.9	97.2
11	0.0299	96.3	97.9
12	0.0299	97.0	98.2
13	0.0299	96.3	98.1
14	0.0299	96.8	98.5
15	0.0299	97.2	101.2
16	0.0345	97.4	99.4
17	0.0345	97.6	98.5
18	0.0345	96.0	98.7
19	0.0490	95.2	96.9
20	0.0490	94.7	96.3
		av. = 96.2, $\sigma = \pm 1.4\%$	av. = 98.3, $\sigma = \pm 2.0\%$

Table XVIII. $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ Stoichiometric Results

Run Number	Initial $NaOSi\phi_3$ and $(\underline{n}\text{-}C_4H_9)_2SnCl_2$ concns. (g. equiv./l)	Sodium chloride yield, (%)	$(\underline{n}\text{-}C_4H_9)_2Sn(\overline{O}Si\phi_3)_2$ yield, (%)
21	0.0127	97.6	95.4
22	0.0127	---	97.1
23	0.0127	98.0	96.6
24	0.0134	---	88.8
25	0.0134	94.6	90.2
26	0.0134	95.6	91.4
27	0.0147	95.2	96.9
28	0.0147	100.9	96.2
29	0.0147	99.8	101.4
30	0.0147	99.7	99.8
31	0.026	95.8	89.5
32	0.026	96.8	89.3
33	0.026	96.7	93.6
38	0.0490	94.6	76.1
39	0.0490	95.1	71.4
40	0.0490	94.9	90.6
41	0.0491	96.8	96.2
42	0.0492	97.3	97.1
43	0.0492	97.9	100.0
44	0.0492	98.3	97.5
		av. = 97.0, $\sigma = \pm$ 1.9%	av. = 92.8, $\sigma = \pm$ 7.6%

Table XIX. $(CH_3)_2Sn(OSi\phi_3)_2$ Stoichiometric Results

Run Number	Initial $NaOSi\phi_3$ and $(CH_3)_2SnCl_2$ Concns. (g. equiv./l)	Sodium chloride yield (%)	$(CH_3)_2Sn(OSi\phi_3)_2$ yield. (%)
57	0.0127	--	88.5
60	0.0134	--	93.2
61	0.0134	95.41	94.2
62	0.0134	--	82.7
64	0.0136	99.01	97.8
65	0.0136	98.63	98.7
66	0.0136	90.91	87.1
68	0.0260	96.92	96.4
69	0.0260	97.23	96.4
78	0.0490	94.67	97.0
		av. =	93.2, $\sigma = \pm 5.3$

There is no evidence significant side reactions occurred. Although a few relatively low $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ and $(CH_3)_2Sn(OSi\phi_3)_2$ yields were observed, a frequency plot of data from 42 runs (Figure 6) shows the results cluster about a central value of 96%. Since the $NaOSi\phi_3$ used was only 96-98% pure, this is the expected range for total consumption of reactants. A reasonably symmetrical spread exists around the central value with small deviations occurring more frequently than large ones. Most of the relatively small deviations can be attributed to errors in the spectrophotometric procedure. A few runs (~20%) had yields of less than 90%. Thus, a systematic error appears to be responsible for the larger variations in $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ yields. In view of the experimental procedure employed in this study, it is postulated that the error results from stoichiometric imbalance of reactants.

The above hypothesis was tested by making several runs in which 0.859 milliequivalent of $NaOSi\phi_3$ was reacted with 0.926 milliequivalent of $(\underline{n}\text{-}C_4H_9)_2SnCl_2$. Results in Table XX show the average sodium chloride recovery was 90.5% while the average $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ yield was 85.3%. These yields are based on the $(\underline{n}\text{-}C_4H_9)_2SnCl_2$ added and are what would be expected if $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ is formed by a two-step reaction as

$$(\underline{n}\text{-}C_4H_9)_2SnCl_2 + NaOSi\phi_3 \longrightarrow (\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)Cl + NaCl$$

$$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)Cl + NaOSi\phi_3 \longrightarrow (\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2 + NaCl$$

The relation between $R'_2Sn(OSiR_3)_2$ yield and $NaOSiR_3$ deficiency for such a process (Figure 7) shows that an 85.7% $(R'_2Sn(OSiR_3)_2$ yield should be obtained for a 7.2% $NaOSiR_3$ deficiency. The experimentally determined 85.3% $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ yield is in excellent agreement with the theoretical value. Likewise, the 90.5% sodium chloride recovery agrees well with the expected value of 92.8%.

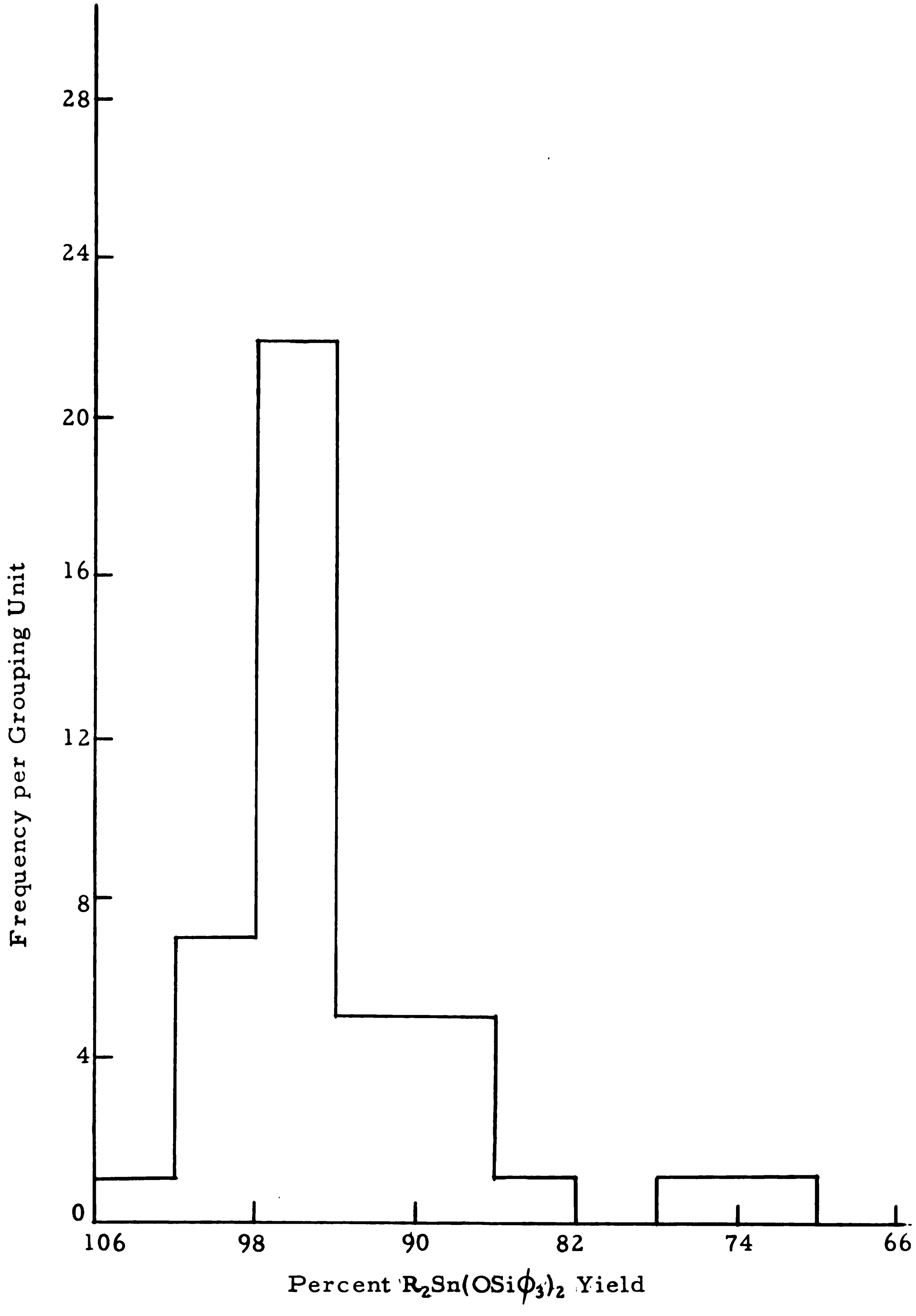


Figure 6. Histogram Showing Frequency of Experimentally Determined $R_2Sn(OSi\phi_3)_2$ Yields.

Table XX. Stoichiometric Results for $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ Formed Using A Known Imbalance of Reactants

Initial $NaOSi\phi_3$ concn. (g. equiv. /l)	Initial $(\underline{n}\text{-}C_4H_9)_2SnCl_2$ concn. (g. equiv. /l)	Sodium chloride yield (%)	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ yield, (%)
0.0430	0.0463	89.4	84.0
0.0430	0.0463	90.3	87.1
0.0430	0.0463	90.6	83.5
0.0430	0.0463	91.6	86.6
		av. = 90.5	av. = 85.3

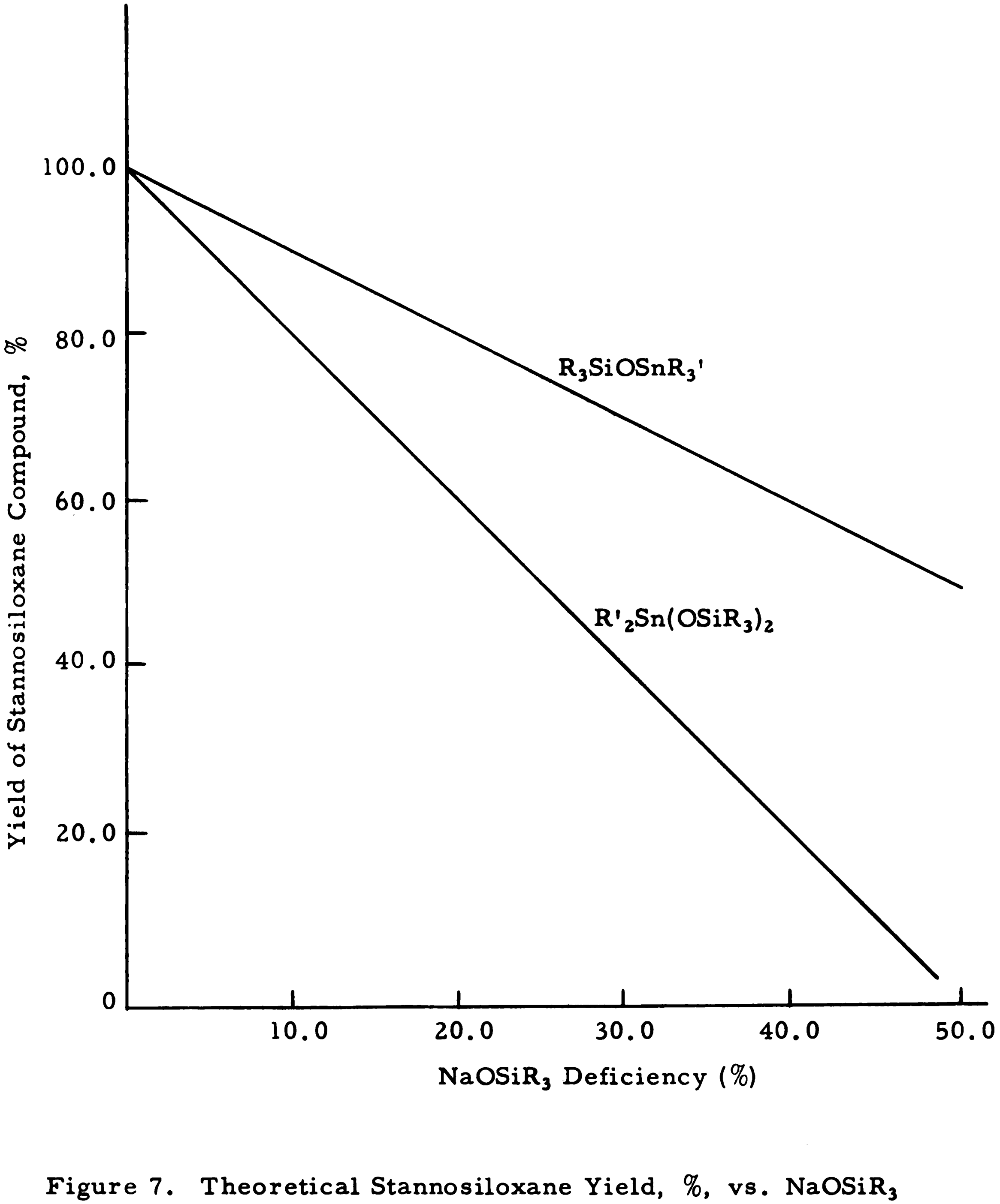


Figure 7. Theoretical Stannosiloxane Yield, %, vs. $NaOSiR_3$ Deficiency, %, for $R_3SiOSnR_3'$ and $R_2'Sn(OSiR_3)_2$.

Included in Figure 7 is a plot of $R_3SiOSnR_3'$ yield versus $NaOSiR_3$ deficiency. This shows that $R_2'Sn(OSiR_3)_2$ yields are twice as sensitive to $NaOSiR_3$ deficiencies as $R_3SiOSnR_3'$ yields. A five percent $NaOSi\phi_3$ deficiency will cause a ten percent decrease in $R_2Sn(OSi\phi_3)_2$ yield and only a five percent drop in $\phi_3SiOSn\phi_3$ yield. From Figure 6, it can be seen that errors of this magnitude could account for an overwhelming majority of the reported low yields. Since such errors could easily arise in the preparation and handling of the reactant solutions and by variation in $NaOSi\phi_3$ purity (96-98%), it was concluded stoichiometric imbalance of the reactants caused the major observed variations in $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ and $(CH_3)_2Sn(OSi\phi_3)_2$ yields. Particularly poor runs 38, 39, and 62 are attributed to gross procedural errors. If these runs are neglected, the standard deviation for $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ and $(CH_3)_2Sn(OSi\phi_3)_2$, ± 4.6 and ± 4.1% respectively, are approximately twice as great as that for $\phi_3SiOSn\phi_3$ (± 2.0%). This is further evidence that variation of stannosiloxane yields is due to stoichiometric imbalance of reactants.

The stoichiometric data discussed to this point were obtained for $NaOSi\phi_3$-organotin chloride reactions carried out in reagent grade benzene which had been fractionally crystallized and distilled over calcium hydride. In order to determine if such highly purified benzene was actually necessary, several runs were carried out in untreated reagent grade benzene. Results in Table XXI show that quantitative yields were obtained in all cases. This indicates that extremely pure benzene is not required for quantitative stannosiloxane formation.

The data in Appendix E show that sodium chloride formation is rapid when stoichiometric amounts of $NaOSi\phi_3$ are mixed in benzene with ϕ_3SnCl, $(CH_3)_2SnCl_2$, $(\underline{n}\text{-}C_4H_9)_2SnCl_2$, or ϕ_2SnCl_2. Representative data have been plotted in Figure 8. Since the $NaOSi\phi_3$ used in this study was 96-98% pure, the observed sodium chloride recoveries correspond to

Table XXI. Stoichiometric Results for $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ Formed in Reagent Grade Benzene

Run Number	Initial reactant concn. (g. equiv. /l)	Sodium chloride yield, (%)	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ yield, (%)
45	0.0302	97.2	95.3
46	0.0302	98.2	100.4
47	0.0302	98.2	97.5
48	0.0302	98.4	98.4
49	0.0359	92.6	94.9
50	0.0359	96.7	95.5
51	0.0359	96.6	96.7
52	0.0359	96.9	94.7

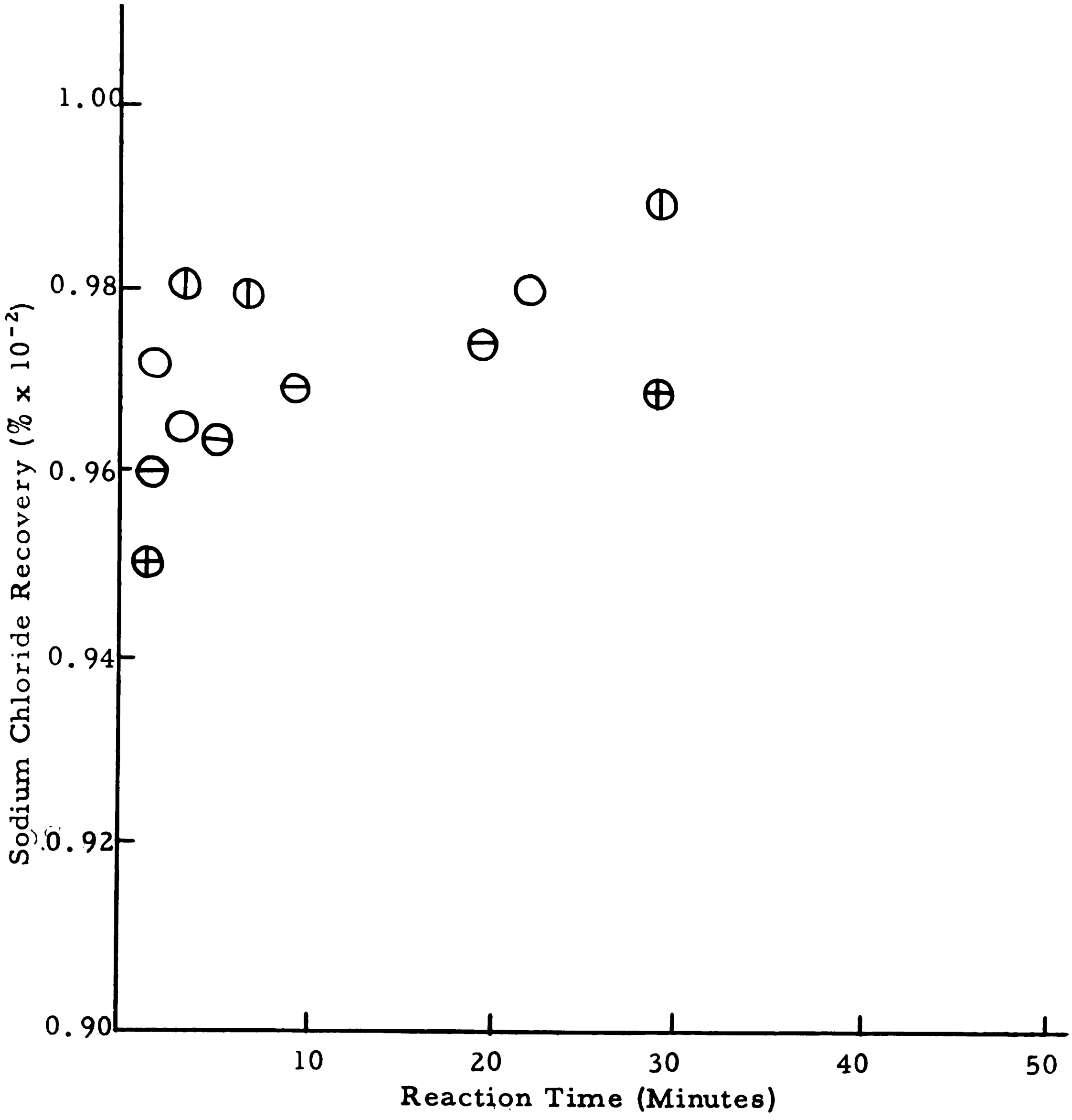


Figure 8. Sodium Chloride Recovery vs. Reaction Time Θ, 0.0299g. equivalent/l NaOSiϕ_3 and ϕ_3SnCl; O, 0.0492 g. equivalent/l NaOSiϕ_3 and $(\underline{n}\text{-}C_4H_9)_2SnCl_2$; Φ, 0.0299 g. equivalent/l NaOSiO$_3$ and $(\bar{C}H_3)_2SnCl_2$; ⊕, 0.0299 g, equivalent/l NaOSiϕ_3 and O_2SnCl_2.

total $NaOSi\phi_3$ consumption. Variation in the sodium chloride yields is within experimental error.

The rapid rate of sodium chloride formation found in this study indicates $NaOSi\phi_3$-organotin chloride condensation processes carried out at room temperature in benzene are extremely fast. Such reactions are complete in less than a minute so quantitative rate data could not be obtained. Although steric and thermal factors may slow the rate of reaction, rapid reaction techniques originally developed by Hartridge and Roughton (49) seem to offer the best approach to obtaining quantitative rate data.

Since quantitative rate measurements were not made, elucidation of a reaction mechanism for the $NaOSi\phi_3$-organotin chloride condensation process in benzene is not possible. However, certain inferences may be drawn from the stoichiometric and qualitative rate data which were obtained. One of these is that pure $NaOSi\phi_3$ will react in benzene with a stoichiometric amount of R_3SnCl or R_2SnCl_2 to give quantitative yields of the corresponding stannosiloxane compound. Side reactions do not occur under the mild reaction conditions employed in this study. This is significant since conventional polycondensation processes, as discussed in the introduction, must utilize reactions which are free of undesirable side reactions. Extrapolation of the above results to bifunctional systems which are capable of polymer formation might seem precarious, but syntheses of organic condensation polymers are based on simple reactions of multifunctional groups. The fact that these reactions were free of secondary processes was established from studies of the corresponding monofunctional systems. The lack of such knowledge has been one of the handicaps in syntheses of organometallosiloxane polymers. Results of the present investigation indicate the reaction of pure $(NaO)_2Si\phi_2$ with R_2SnCl_2 in an aprotic solvent should yield stannosiloxane polymers having a regular alternating (Si-O-Sn-O) structure. If cyclic compounds are formed, it should be possible to isolate and identify these. The important point is Si-O-Si or Sn-O-Sn bonds should not be formed by various side reactions under normal reaction conditions if pure reactants are employed.

It is significant that the reaction of $NaOSi\phi_3$ with organotin chlorides in benzene is extremely fast and irreversible. The sodium chloride by-product precipitates immediately thereby forcing the reaction to completion. This distinguishes such reactions from those commonly employed to synthesize organic condensation polymers. Organic polycondensation processes, in general, have utilized slow, reversible organic reactions which require elevated temperatures and reduced pressure for high polymer formation. A notable exception is the interfacial polycondensation technique which has recently been developed (50, 51). In this method a fast, irreversible polymerization of two fast-reacting intermediates occurs near the interface between phases of a heterogeneous liquid system (50, 51). Characteristic features of ordinary melt and interfacial polycondensation processes are compared in Table XXII (50). The interfacial method is obviously the simplest since impurities, stoichiometric imbalance of reactants, and even side reactions do not necessarily limit polymer formation. All of these factors drastically limit the molecular weight of polymers formed by the melt condensation process.

Since reactions ordinarily used in interfacial polycondensations are similar to the $NaOSi\phi_3$-organotin chloride reaction (fast and irreversible), it appears that regular alternating stannosiloxane polymers could be prepared by the interfacial method. The only difficulty seems to be lack of a suitable heterogeneous solvent system since relatively pure $(NaO)_2Si\phi_2$ has already been isolated.

Table XXII. Comparison of Interfacial and Melt Polycondensation

	Interfacial	Melt
Intermediates		
Purity	moderate to high (>90%)	high (>98%)
Balance	unnecessary	necessary
Stability to heat	unnecessary	necessary
Polymerization conditions		
Time	several minutes	several hours
Temperature	0-40°C	>200°C
Pressure	atmospheric	high and low
Equipment	simple, open	special, sealed
Products		
Yield	low to high	high
Structure	unlimited	limited by stability to heat and fusibility

C. Polymer Formation

Several stannosiloxane polymers were synthesized by the *in situ* condensation of $(NaO)_2Si\phi_2$ with $(\underline{n}\text{-}C_4H_9)_2SnCl_2$. The polymers have not been fully characterized as to their hydrolytic and thermal stability, molecular weight, or various other physical properties. Attention was focused on determining if the silanolate-organotin chloride reaction involving bifunctional reactants proceeded in the same manner as the monofunctional systems. The polymerizations were carried out under a variety of reaction conditions. Complete material balances were established about each reaction system and the sodium chloride recovery data taken as a measure of the extent of reaction.

The results (Table XII) show there is essentially no difference in the extent of reaction of each polymerization process. Similar sodium chloride recoveries were obtained for the polymerization carried out at -14°C for two hours and that carried out at reflux temperature for 24 hours. These data imply the *in situ* reaction of $(NaO)_2Si\phi_2$ with $(\underline{n}\text{-}C_4H_9)_2SnCl_2$ is rapid.

Undesirable side reactions in the *in situ* $(NaO)_2Si\phi_2\text{-}(\underline{n}\text{-}C_4H_9)_2SnCl_2$ polycondensation process were detected by fractionating the bulk stannosiloxane polymers into a methanol-soluble and methanol-insoluble fractions as outlined previously. Carbon, hydrogen, and chlorine analyses for each methanol-insoluble fraction are shown in Table XXIII. Calculated carbon-hydrogen values are for the $[O\text{-}Si\phi_2\text{-}O\text{-}Sn(\underline{n}\text{-}C_4H_9)_2]$ unit.

Although none of the fractions had carbon-hydrogen analyses which agreed well with the calculated values, carbon-hydrogen analyses for the ϕ-Bu I and ϕ-Bu II fractions are extremely close. This indicates, but does not prove, the ϕ-Bu I and ϕ-Bu II polymerizations were relatively free of side reactions. In contrast, carbon-hydrogen analyses for the ϕ-Bu III and ϕ-Bu IV fractions differ significantly from the calculated

Table XXIII. **Analytical Data for Methanol-Insoluble Stannosiloxane Polymer Fractions**

	Analytical				
	Calculated		Found		
Polymer	C(%)	H(%)	C(%)	H(%)	Cl(%)
ϕ-Bu I	53.73	6.27	53.33	6.20	0.0
			53.22	6.24	
ϕ-Bu II	53.73	6.27	53.43	6.36	0.0
			53.37	6.25	
ϕ-Bu III	53.73	6.27	48.42	6.60	0.0
			48.62	6.52	
ϕ-Bu IV	53.73	6.27	44.64	6.86	0.0
			44.72	6.92	

values. In these cases the Si-Sn ratio is < 1 indicating significant side reactions have occurred. It is interesting to note reaction times for ϕ-Bu III and ϕ-Bu IV are much greater than those for ϕ-Bu I and ϕ-Bu II.

Infrared spectra for all methanol-soluble fractions were essentially identical (a representative spectra is shown in Appendix D). Strong absorption from 9.0 to 10.5 μ is due to several overlapping peaks. The peak at 9.0 μ is the Si-O stretch bond while that at 10.4 μ is attributed to the Si-O-Sn bond. Absorption at 9.3-9.6 μ is probably due to the Si-O-Si bond.

The above results imply the *in situ* $(NaO)_2Si\phi_2$-$(\underline{n}\text{-}C_4H_9)_2SnCl_2$ polymerization process is rapid and yields polymers which contain Si-O-Sn bonds. However, further conclusions about these polymers can not be made at present since they have not been properly characterized. Such characterization will be the subject of a future study. In addition it will be necessary to perform the polymerization with highly purified monomers under conditions more conducive to high polymer formation than those attempted to date.

IV. SUMMARY

A series of stannosiloxane compounds has been prepared by the condensation of sodium triphenylsilanolate with various organotin chlorides in benzene. Infrared and elemental analyses were employed to characterize the reaction products.

The stoichiometry of the reaction of sodium triphenylsilanolate with triphenyltin chloride, dimethyltin dichloride, and dibutyltin dichloride in benzene has been established. Sodium chloride by-product yields were obtained by standard silver nitrate titration. Stannosiloxane yields were determined spectrophotometrically using the characteristic Si-O-Sn peak for identification. Results obtained using these techniques show the sodium chloride-organotin chloride condensation reaction in benzene goes to completion and is free of significant side reactions.

Sodium chloride formation has been found to be rapid when sodium triphenylsilanolate is caused to react at room temperature in benzene with a stoichiometric amount of an organotin chloride. Such reactions are complete in less than a minute, so quantitative rate data could not be obtained. For this reason, a mechanism can not be postulated for the sodium triphenylsilanolate-organotin chloride condensation process in benzene. However, the lack of side reactions in such processes is significant since this implies the reaction of pure $(NaO)_2Si\phi_2$ with organotin dichlorides in an aprotic solvent will yield high molecular weight stannosiloxane polymers having a regular alternating (-Si-O-Sn-) structure.

Several stannosiloxane polymers have been prepared under a wide range of reaction conditions by the in situ condensation of $(NaO)_2Si\phi_2$ with dibutyltin dichloride. The polymers were not fully characterized, but it has been established that the polymerization process is rapid. Highly purified $(NaO)_2Si\phi_2$, which is soluble in absolute ethanol, has been isolated and will be used in future stannosiloxane polymerizations.

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APPENDICES

APPENDIX A

Reaction Conditions and Stoichiometric Data for $\phi_3SiOSn\phi_3$, $(CH_3)_2Sn(OSi\phi_3)_2$, and $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ Formation.

Run Number	Compound	Initial $NaOSi\phi_3$ and R_3SnCl or R_2SnCl_2 conc. (g. equiv./1.)	Reaction time (min.)	Recovered sodium chloride (g)	Calcd. sodium chloride (g)	Benzene soluble solids recovered (g)	Calcd. total solids (g)	Total solids recovery (%)
1	$\phi_3SiOSn\phi_3$	0.00783	2.1	0.0174	0.0183	--	--	--
2	$\phi_3SiOSn\phi_3$	0.00783	2.4	0.0173	0.0183	--	--	--
3	$\phi_3SiOSn\phi_3$	0.00783	5.6	0.0174	0.0183	--	--	--
4	$\phi_3SiOSn\phi_3$	0.00783	24.7	0.0175	0.0183	--	--	--
5	$\phi_3SiOSn\phi_3$	0.0127	1.1	0.0143	0.0149	0.1578	0.1736	99.1
6	$\phi_3SiOSn\phi_3$	0.0127	51.3	0.0148	0.0149	0.1595	0.1736	100.4
7	$\phi_3SiOSn\phi_3$	0.0127	2796.0	0.0146	0.0149	0.1571	0.1736	98.9
8	$\phi_3SiOSn\phi_3$	0.0134	0.9	0.0147	0.0157	0.1657	0.1831	98.53
9	$\phi_3SiOSn\phi_3$	0.0134	5.4	0.0148	0.0157	0.1655	0.1831	98.47
10	$\phi_3SiOSn\phi_3$	0.0134	1447.0	0.0149	0.0157	0.1673	0.1831	99.51
11	$\phi_3SiOSn\phi_3$	0.0299	0.8	0.0168	0.0175	--	--	--
12	$\phi_3SiOSn\phi_3$	0.0299	0.8	0.0170	0.0175	--	--	--
13	$\phi_3SiOSn\phi_3$	0.0299	5.6	0.0169	0.0175	--	--	--
14	$\phi_3SiOSn\phi_3$	0.0299	9.3	0.0170	0.0175	--	--	--
15	$\phi_3SiOSn\phi_3$	0.0299	27.5	0.0168	0.0175	--	--	--
16	$\phi_3SiOSn\phi_3$	0.0345	0.9	0.0201	0.0202	0.2131	0.2353	99.11
17	$\phi_3SiOSn\phi_3$	0.0345	27.8	0.0199	0.0202	0.1990	0.2353	93.03
18	$\phi_3SiOSn\phi_3$	0.0345	2994.0	0.0199	0.0202	0.2121	0.2353	98.60
19	$\phi_3SiOSn\phi_3$	0.0490	54.7	0.0272	0.0286	0.2991	0.3343	97.61
20	$\phi_3SiOSn\phi_3$	0.0490	2225.0	0.0271	0.0286	0.2996	0.3343	97.73
21	$(\underline{n}-C_4H_9)_2Sn(OSi\phi_3)_2$	0.0127	1.3	--	0.0149	0.0997	0.1143	--
22	$(\underline{n}-C_4H_9)_2Sn(OSi\phi_3)_2$	0.0127	54.3	0.0145	0.0149	0.0988	0.1143	99.13
23	$(\underline{n}-C_4H_9)_2Sn(OSi\phi_3)_2$	0.0127	2978.0	0.0146	0.0149	0.0982	0.1143	98.69

Continued

Run Number	Compound	Initial $NaOSi\phi_3$ and R_3SnCl or R_2SnCl_2 conc. (g. equiv./l.)	Reaction time (min.)	Recovered sodium chloride (g)	Calcd. sodium chloride (g)	Benzene soluble solids recovered (g)	Calcd. total solids (g)	Total solids recovery (%)
24	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0134	0.7	--	0.0157	--	0.1207	--
25	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0134	54.5	0.0148	0.0157	0.1063	0.1207	100.33
26	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0134	8878.0	0.0150	0.0157	0.1033	0.1207	98.01
27	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	4.0	0.0164	0.0172	0.1233	0.1421	98.31
28	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	9.0	0.0174	0.0172	0.1229	0.1421	98.73
29	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	148.1	0.0172	0.0172	0.1217	0.1421	97.73
30	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	1207.0	0.0172	0.0172	0.1226	0.1421	98.38
31	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0260	1.1	0.0146	0.0152	0.1019	0.1170	100.85
32	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0260	44.8	0.0147	0.0152	0.1033	0.1170	99.57
33	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0260	2153.0	0.0147	0.0152	0.1016	0.1170	99.40
34	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	0.6	0.0201	0.0207	--	--	--
35	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	0.9	0.0200	0.0207	--	--	--
36	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	28.1	0.0201	0.0207	--	--	--
37	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	165.0	0.0205	0.0207	--	--	--
38	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0490	0.8	0.0270	0.0286	0.1971	0.2202	99.68
39	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0490	50.4	0.0272	0.0286	0.1991	0.2202	101.77
40	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0490	1560.0	0.0271	0.0286	0.1924	0.2202	102.77
41	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	1.1	0.0279	0.0288	0.1598	0.2213	84.82
42	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	7.0	0.0280	0.0288	0.1916	0.2213	99.23
43	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	21.5	0.0282	0.0288	0.1907	0.2213	98.92
44	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	65.4	0.0283	0.0288	0.1905	0.2213	98.87
45	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	0.6	0.0172	0.0177	0.1106	0.1360	93.97
46	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	10.3	0.0173	0.0177	0.1169	0.1360	98.67
47	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	41.8	0.0173	0.0177	0.1188	0.1360	100.07
48	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	853.0	0.0174	0.0177	0.1179	0.1360	99.48

Continued

Run Number	Compound	Initial $NaOSi\phi_3$ and R_3SnCl or R_2SnCl_2 conc. (g.equiv./l.)	Reaction time (min.)	Recovered sodium chloride (g)	Calcd. sodium chloride (g)	Benzene soluble solids recovered (g)	Calcd. total solids (g)	Total solids recovery (%)
49	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	0.7	0.0194	0.0210	0.1368	0.1614	96.78
50	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	14.7	0.0203	0.0210	0.1374	0.1614	97.71
51	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	64.4	0.0203	0.0210	0.1377	0.1614	97.89
52	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	352.0	0.0203	0.0210	0.1366	0.1614	97.21
53	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0430*	0.9	0.0242	0.0248	0.1723	0.1983	99.09
54	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0430	10.1	0.0244	0.0248	0.1716	0.1983	98.84
55	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0430	43.6	0.0245	0.0248	0.1731	0.1983	99.65
56	$(\underline{n}\text{-}C_6H_9)_2Sn(OSi\phi_3)_2$	0.0430	825.0	0.0248	0.0248	0.1722	0.1983	99.34
57	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0127	1.3	--	0.0149	0.0889	0.1037	--
58	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0127	85.4	0.0146	0.0149	0.0898	0.1037	100.68
59	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0127	2887.0	--	0.0149	0.0878	0.1037	--
60	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0134	1.8	--	0.0157	0.0935	0.1094	--
61	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0134	58.8	0.0150	0.0157	0.0938	0.1094	99.45
62	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0134	8811.0	--	0.0157	0.0887	0.1094	--
63	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	3.8	0.0156	0.0159	0.0956	0.1108	100.36
64	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	12.5	0.0157	0.0159	0.0954	0.1108	100.27
65	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	61.8	0.0157	0.0159	0.0952	0.1108	100.09
66	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	682.0	0.0145	0.0159	0.0954	0.1108	99.19
67	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0260	0.9	0.0147	0.0152	0.0887	0.1061	97.46
68	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0260	54.6	0.0147	0.0152	0.0893	0.1061	98.02
69	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0260	2795.0	0.0148	0.0152	0.0908	0.1061	99.53
70	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0299	0.9	0.0173	0.0175	--	--	--
71	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0299	1.3	0.0172	0.0175	--	--	--
72	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0299	29.5	0.0347	0.0350	--	--	--

*0.0463 g eq/l $(\underline{n}\text{-}C_4H_9)_2SnCl_2$

Continued

Run Number	Compound	Initial $NaOSi\phi_3$ and R_3SnCl or R_2SnCl_2 conc. (g. equiv./l.)	Reaction time (min.)	Recovered sodium chloride (g)	Calcd. sodium chloride (g)	Benzene soluble solids recovered (g)	Calcd. total solids (g)	Total solids recovery (%)
73	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0345	0.9	0.0198	0.0202	0.1215	0.1452	97.31
74	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0345	87.9	0.0200	0.0202	0.1203	0.1452	96.63
75	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0345	3116.0	---	0.0202	0.1291	0.1452	--
76	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0490	1.0	0.0272	0.0286	0.1711	0.1997	99.30
77	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0490	50.2	0.0273	0.0286	0.1734	0.1997	100.50
78	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0490	2190.0	0.0271	0.0286	0.1711	0.1997	99.25

APPENDIX B

Spectrophotometric Data for $\phi_3SiOSn\phi_3$, $(CH_3)_2Sn(OSi\phi_3)_2$, and $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ Formation.

Run	c_0 (M)	A	c (M)	$c/c_0 \times 10^2$
$\phi_3SiOSn\phi_3$:				
1	0.00872	0.262	0.00850	97.5
2	0.00906	0.268	0.00869	95.9
	0.00906	0.270	0.00875	96.6
3	0.00848	0.257	0.00837	98.7
4	0.00855	0.261	0.00847	99.1
5	0.00813	0.242	0.00786	96.7
6	0.00858	0.266	0.00860	100.2
7	0.00842	0.268	0.00869	103.2
8	0.00845	0.244	0.00791	93.6
9	0.00762	0.233	0.00757	99.3
10	0.00842	0.253	0.00818	97.2
11	0.00780	0.236	0.00765	98.1
12	0.00708	0.213	0.00693	97.9
13	0.00818	0.249	0.00806	98.5
14	0.00829	0.251	0.00814	98.2
15	0.00740	0.230	0.00749	101.2
16	0.00841	0.256	0.00830	98.7
17	0.00855	0.262	0.00850	99.4
18	0.00810	0.246	0.00798	98.5
19	0.00844	0.252	0.00818	96.9
20	0.00880	0.261	0.00847	96.3
$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$:				
21	0.00662	0.339	0.00641	96.8
	0.00662	0.326	0.00617	93.2
	0.00608	0.309	0.00582	95.7
22	0.00811	0.404	0.00762	94.0
	0.00811	0.409	0.00771	95.1
	0.00669	0.353	0.00667	99.7
23	0.00662	0.331	0.00626	94.6
	0.00626	0.327	0.00618	98.7
24	0.00664	0.312	0.00590	88.9
	0.00664	0.311	0.00589	88.7
25	0.00703	0.336	0.00634	90.2
26	0.00636	0.305	0.00578	90.9
	0.00636	0.309	0.00584	91.8

Continued

Run	c_0 ($\underline{M}$)	A	c. ($\underline{M}$)	$c/c_0 \times 10^2$
$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ cont'd:				
27	0.00423	0.217	0.00410	96.9
28	0.00603	0.307	0.00580	96.2
29	0.00659	0.352	0.00666	101.1
	0.00659	0.355	0.00670	101.7
30	0.00613	0.321	0.00608	99.2
	0.00613	0.325	0.00615	100.3
31	0.00620	0.294	0.00555	89.5
32	0.00590	0.281	0.00530	89.3
33	0.00629	0.310	0.00588	93.5
	0.00629	0.311	0.00590	93.8
38	0.00593	0.233	0.00440	74.2
	0.00770	0.319	0.00610	79.2
	0.00770	9.317	0.00590	76.6
39	0.00662	0.246	0.00463	69.9
	0.00698	0.263	0.00497	71.2
	0.00698	0.275	0.00519	74.4
40	0.00809	0.387	0.00730	90.2
	0.00809	0.390	0.00736	91.0
41	0.00728	0.370	0.00700	96.2
42	0.00692	0.356	0.00672	97.1
43	0.00681	0.361	0.00681	100.0
44	0.00731	0.379	0.00713	97.5
45	0.00741	0.374	0.00706	95.3
46	0.00687	0.355	0.00670	97.5
47	0.00687	0.366	0.00690	100.4
48	0.00759	0.395	0.00747	98.4
49	0.00685	0.344	0.00650	94.9
50	0.00694	0.351	0.00663	95.5
51	0.00692	0.354	0.00669	96.7
52	0.00758	0.380	0.00718	94.7
53	0.00774	0.345	0.00650	84.0
54	0.00689	0.317	0.00600	87.1
55	0.00729	0.321	0.00609	83.5
56	0.00669	0.306	0.00579	86.6

Continued

Run	c_0 (M)	A	c, (M)	$c/c_0 \times 10^2$
$(CH_3)_2Sn(OSi\phi_3)_2$:				
57	0.00583	0.201	0.00516	88.5
60	0.00577	0.210	0.00538	93.2
61	0.00584	0.215	0.00526	94.2
62	0.00653	0.211	0.00540	82.7
64	0.00726	0.278	0.00710	97.8
65	0.00607	0.234	0.00579	98.7
66	0.00627	0.212	0.00546	87.1
68	0.00575	0.216	0.00554	96.4
69	0.00580	0.217	0.00559	96.4
78	0.00696	0.263	0.00675	97.0

APPENDIX C

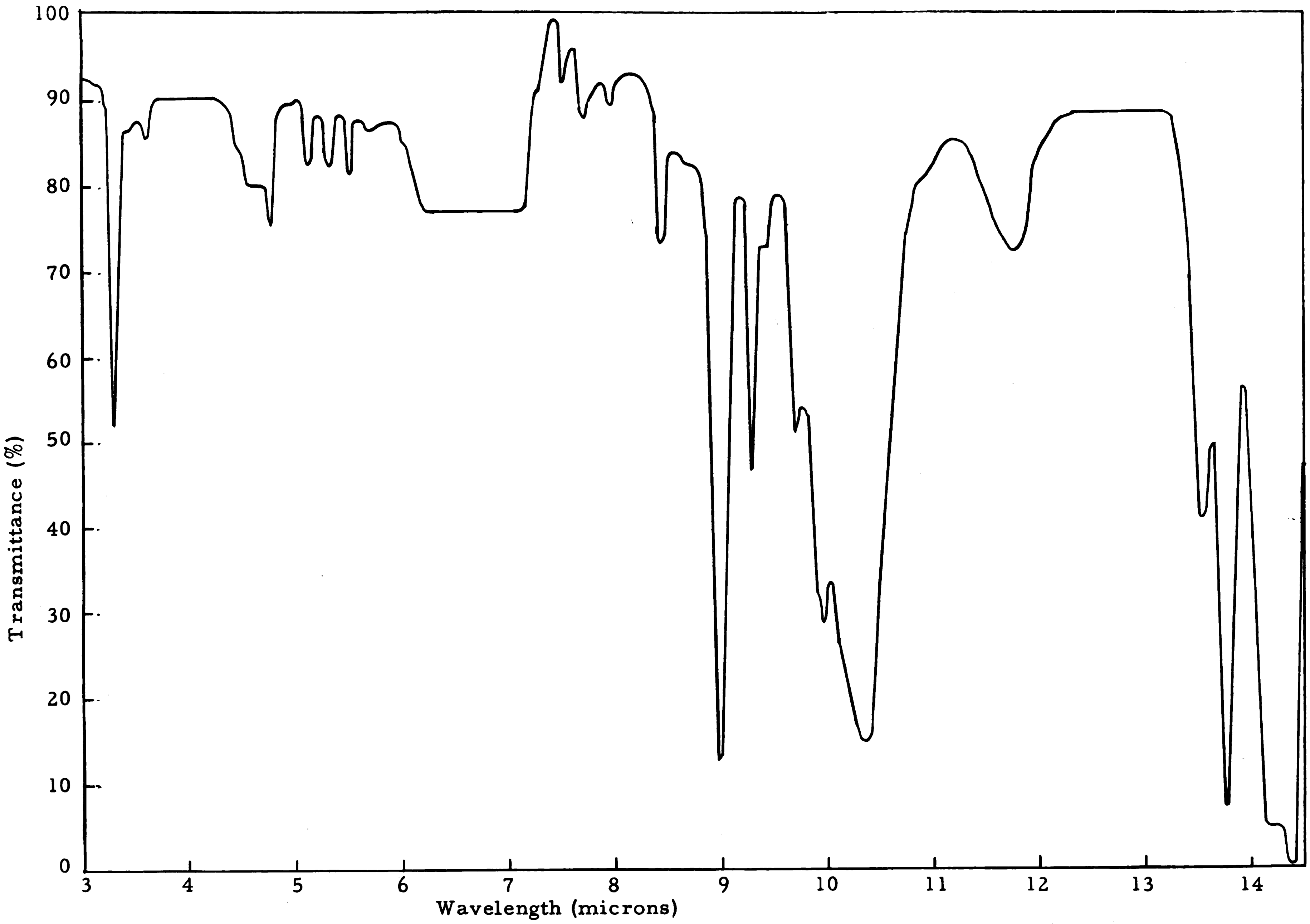
Solubility Characteristics of Stannosiloxane Polymers

Solvent	Polymer Sample		
	ϕ-Bu I		
	(bulk)	(methanol-soluble)	(methanol-insoluble)
Carbon disulfide	ps[*]	s	ss
Isopropanol	i	i	i
N-heptane	i	s	i
Nitrobenzene	ss	s	ps
Benzene	ps	s	ss
Ethylene dichloride	i	s	i
Tetralin	ps	s	ps
	ϕ-Bu II		
	(bulk)	(methanol-soluble)	(methanol-insoluble)
Carbon disulfide	ps	s	ss
Isopropanol	i	i	i
N-heptane	i	s	i
Nitrobenzene	ss	s	ps
Methyl ethyl ketone	ps	s	i
Anisole	ps	s	ps
Acetonitrile	i	ss	i
	ϕ-Bu III		
	(bulk)	(methanol-soluble)	(methanol-insoluble)
Methyl ethyl ketone	ps	s	i
Anisole	ps	s	ps
Acetonitrile	i	ss	i
N-amylacetate	i	s	i
DMF	ss	s	i
Carbon tetrachloride	ps	s	i
Ethyl ether	ps	s	i
	ϕ-Bu IV		
		(precipitated)	(non-precipitated)
N-amyl acetate		--	ss
DMF		i	ps
Carbon tetrachloride		i	ps
Ethyl ether		i	ps
Benzene		ss	ps
Ethylene dichloride		i	ps
Tetralin		ss	ss

[*] s = soluble; ps = partly soluble; ss = slightly soluble; i = insoluble.

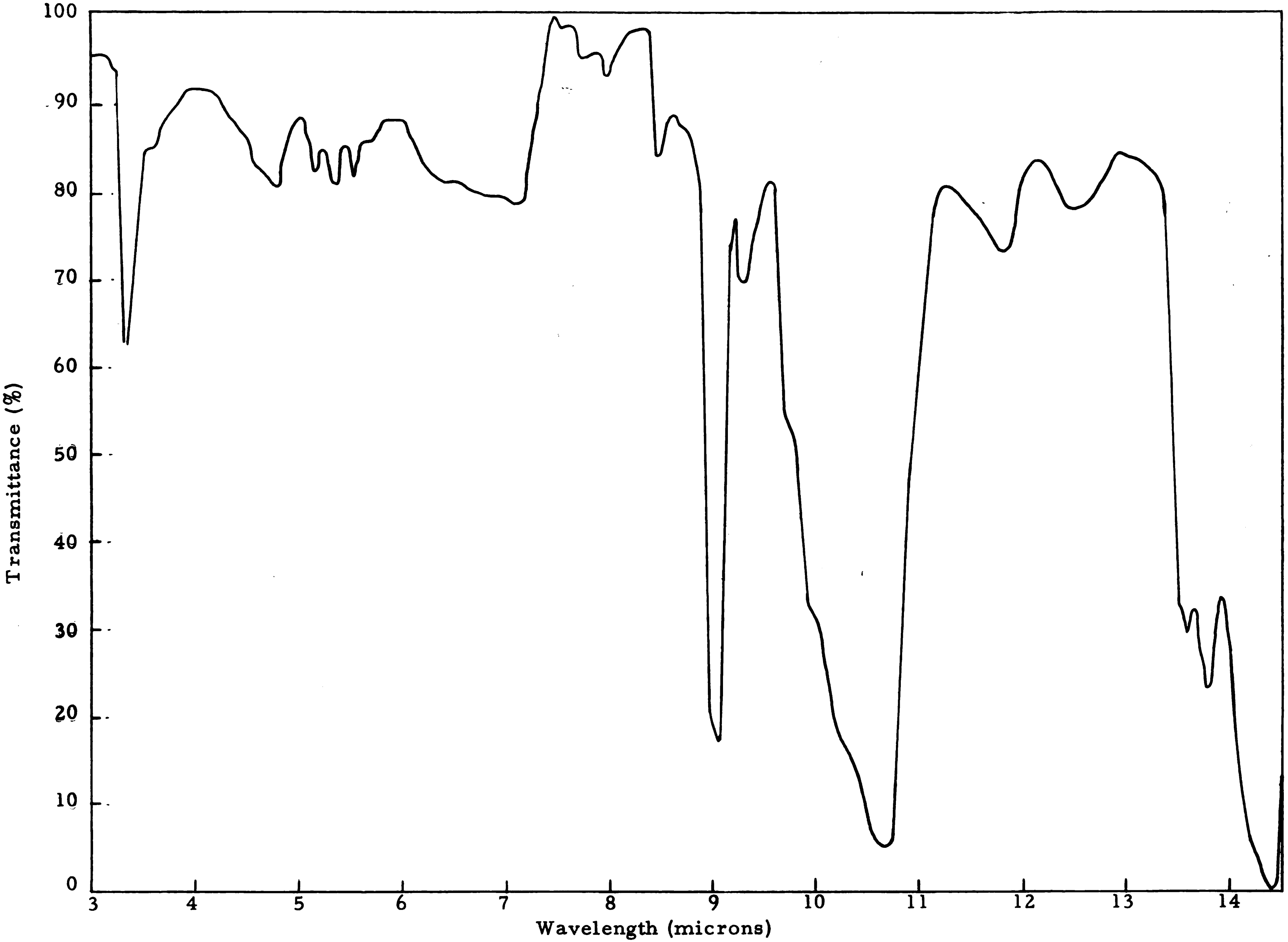
APPENDIX D

Infrared Spectra

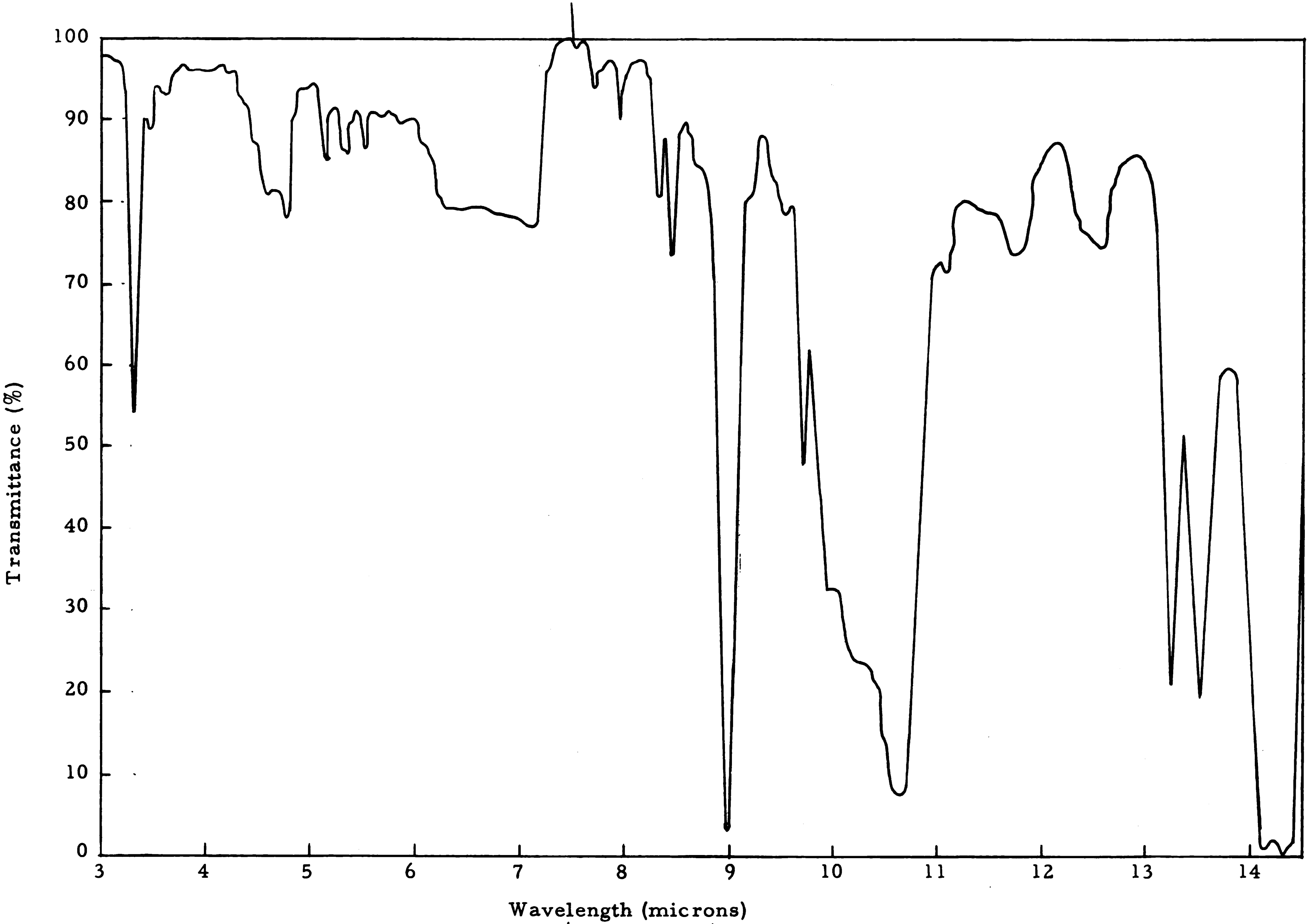


Infrared spectra of $\phi_3SiOSn\phi_3$ in carbon disulfide.

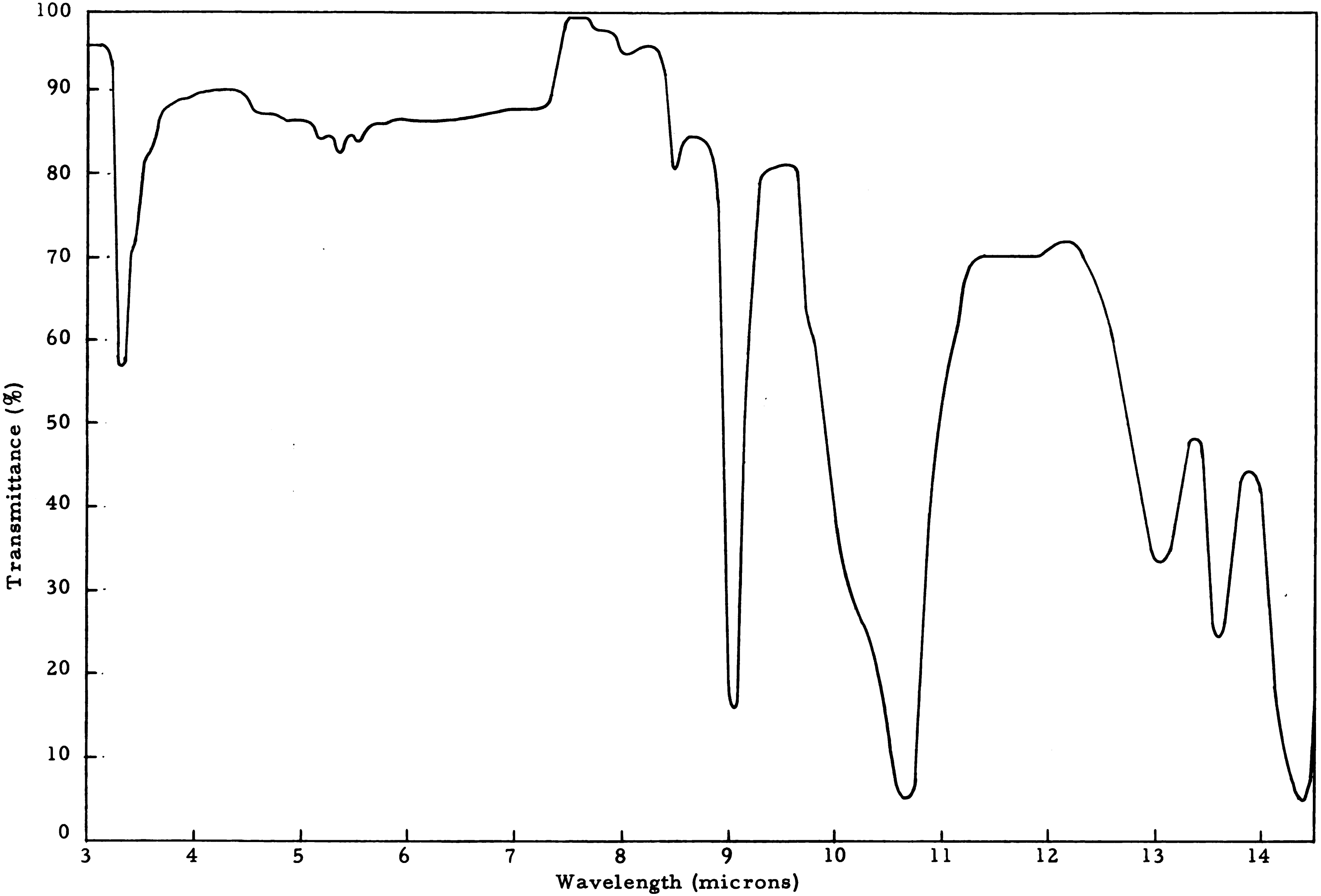

100



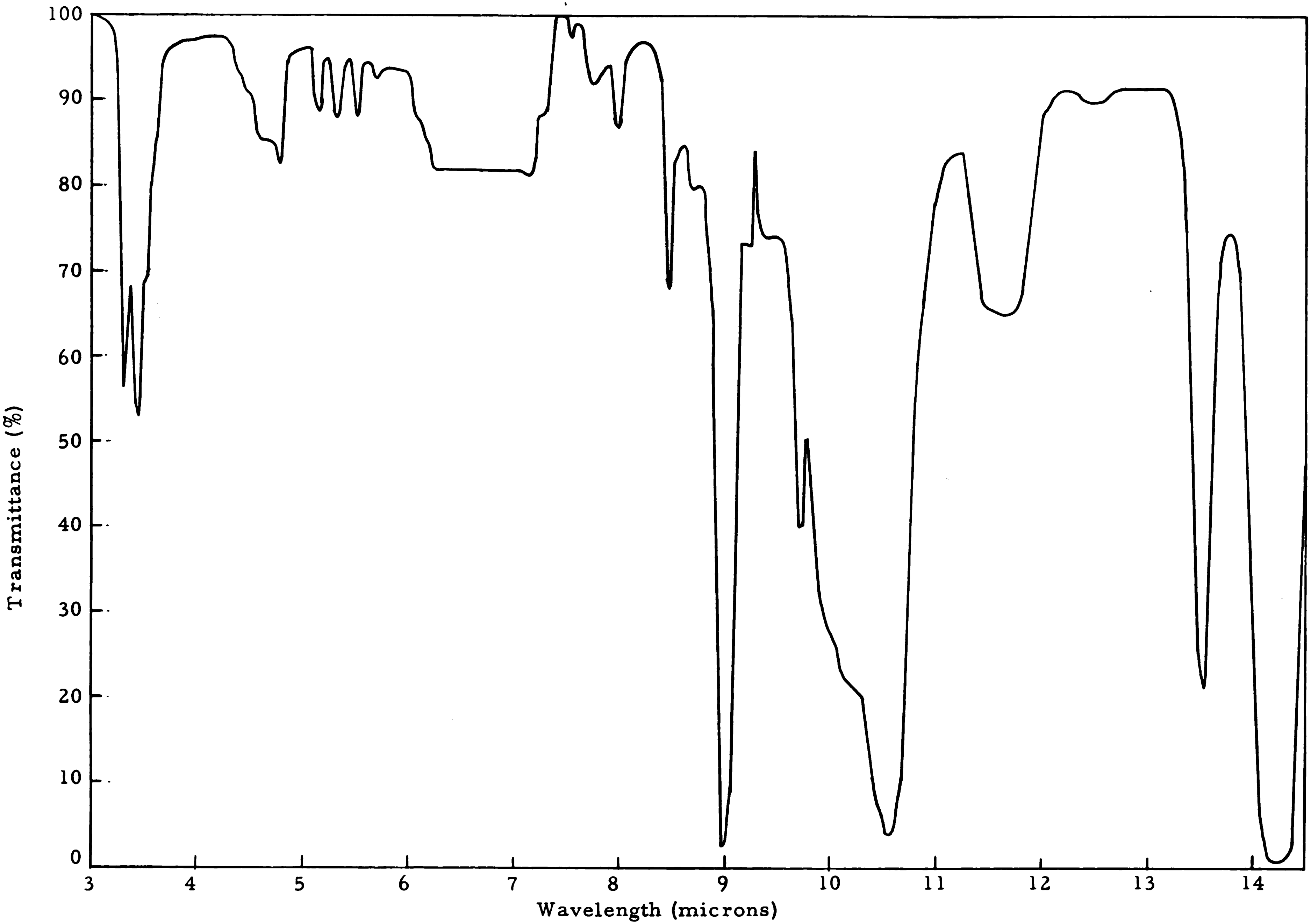
Infrared spectra of $\phi_2Sn(OSi\phi_3)_2$ in carbon disulfide.



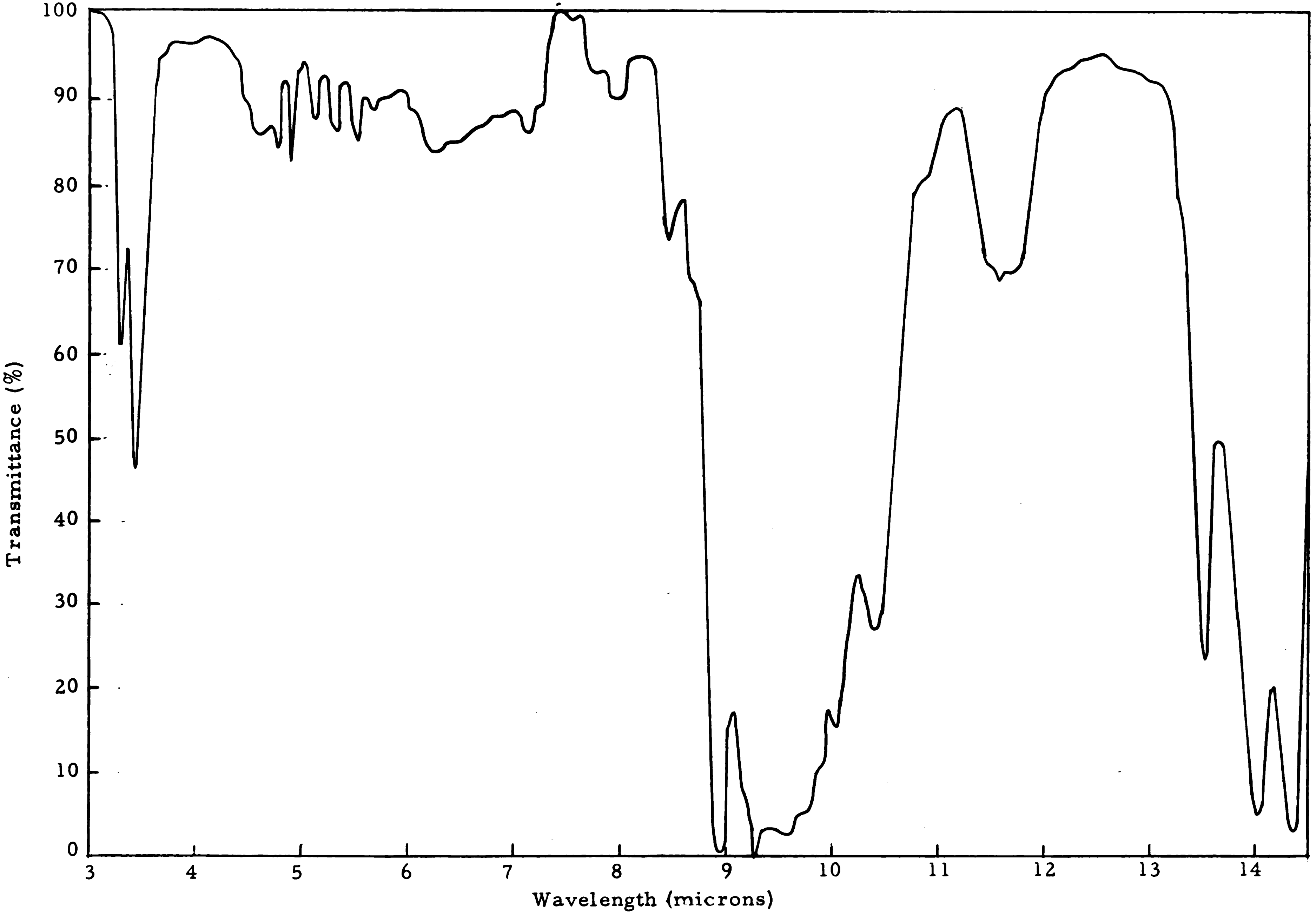
Infrared spectra of $(\phi CH_3)_2Sn(OSi\phi_3)_2$ in carbon disulfide.



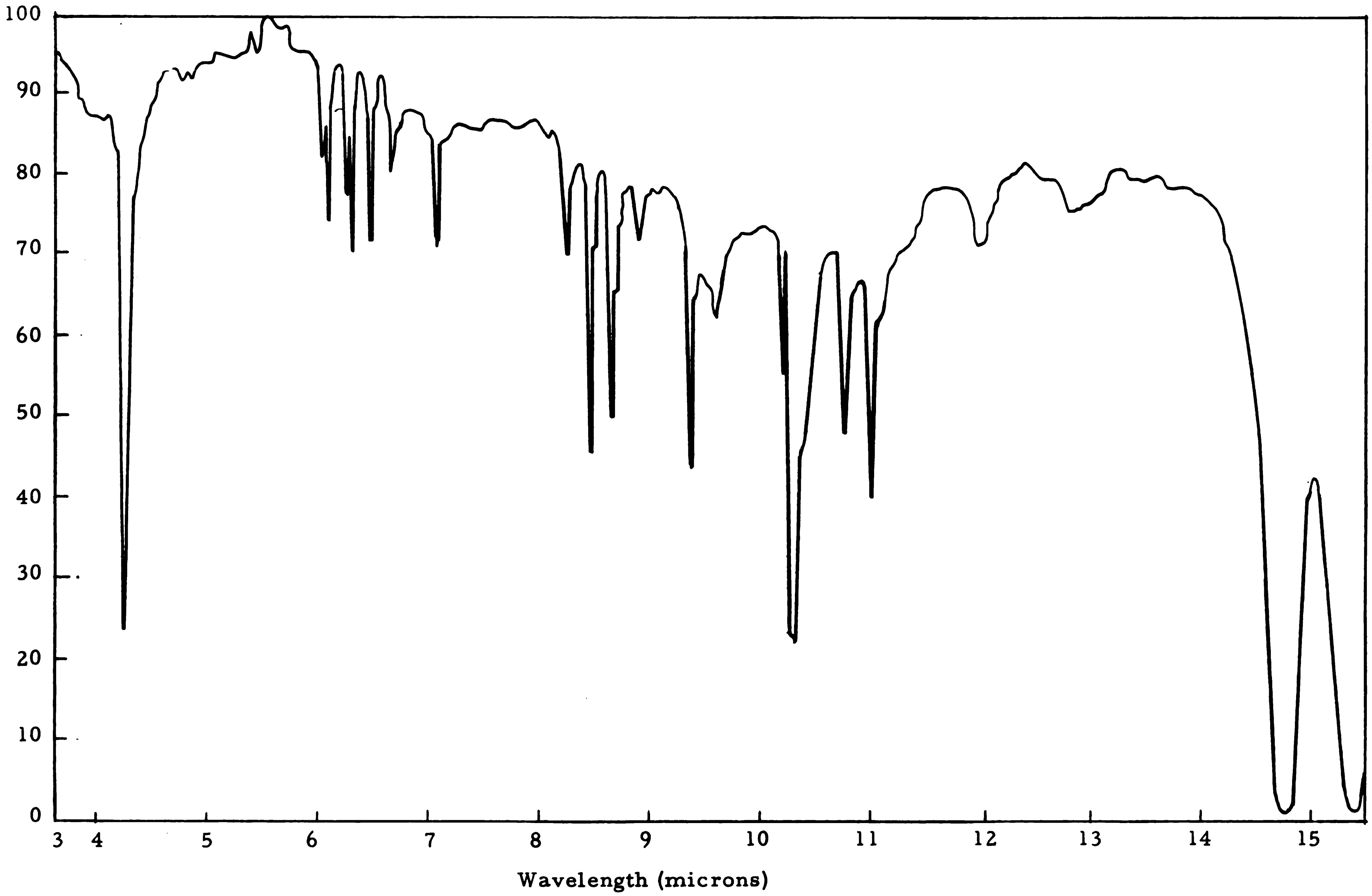
Infrared spectra of $(CH_3)_2Sn(OSi\phi_3)_2$ in carbon disulfide.



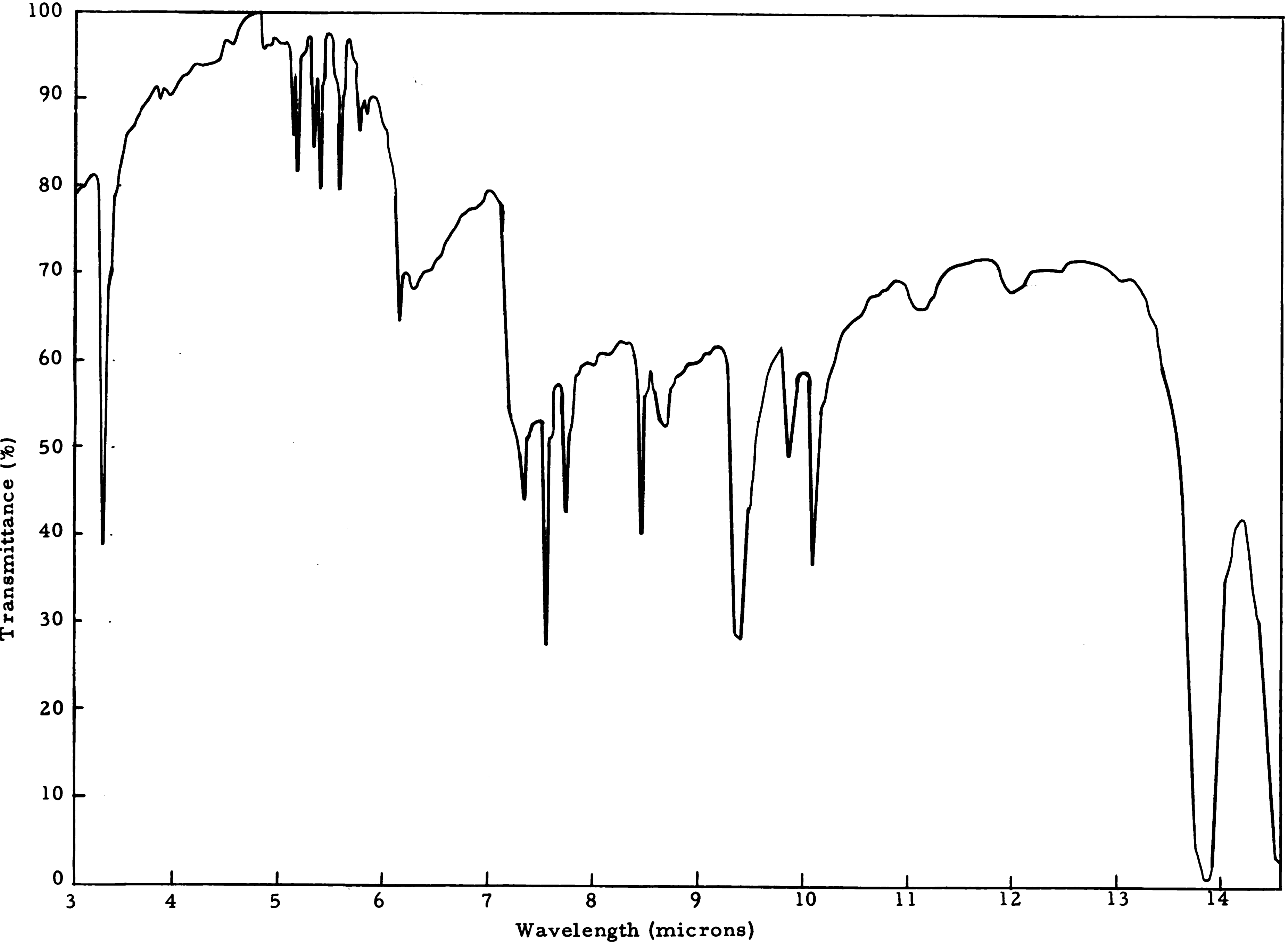
Infrared spectra of $(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ in carbon disulfide.



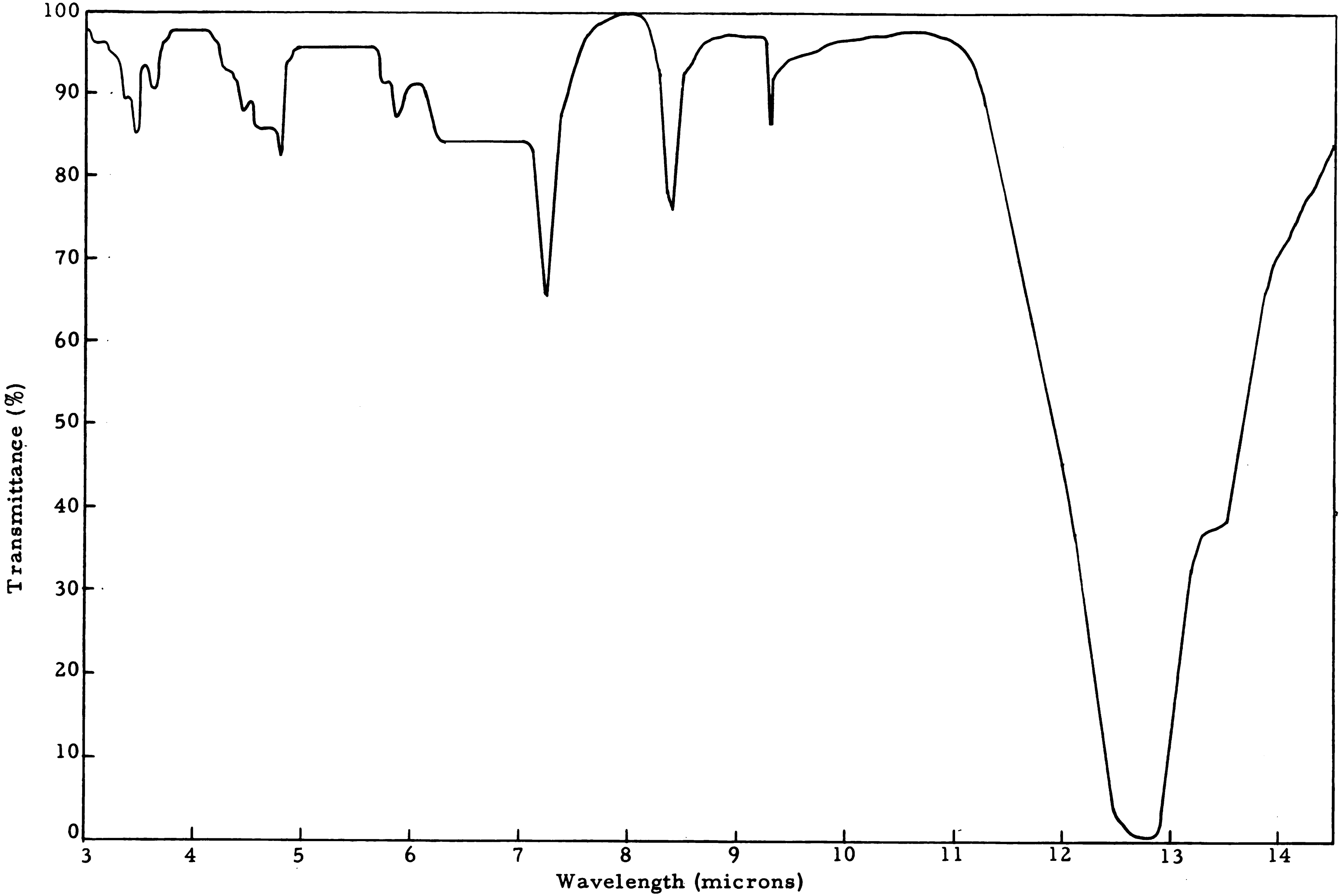
Infrared spectra of methanol-soluble fraction of ϕ-Bu III in carbon disulfide.



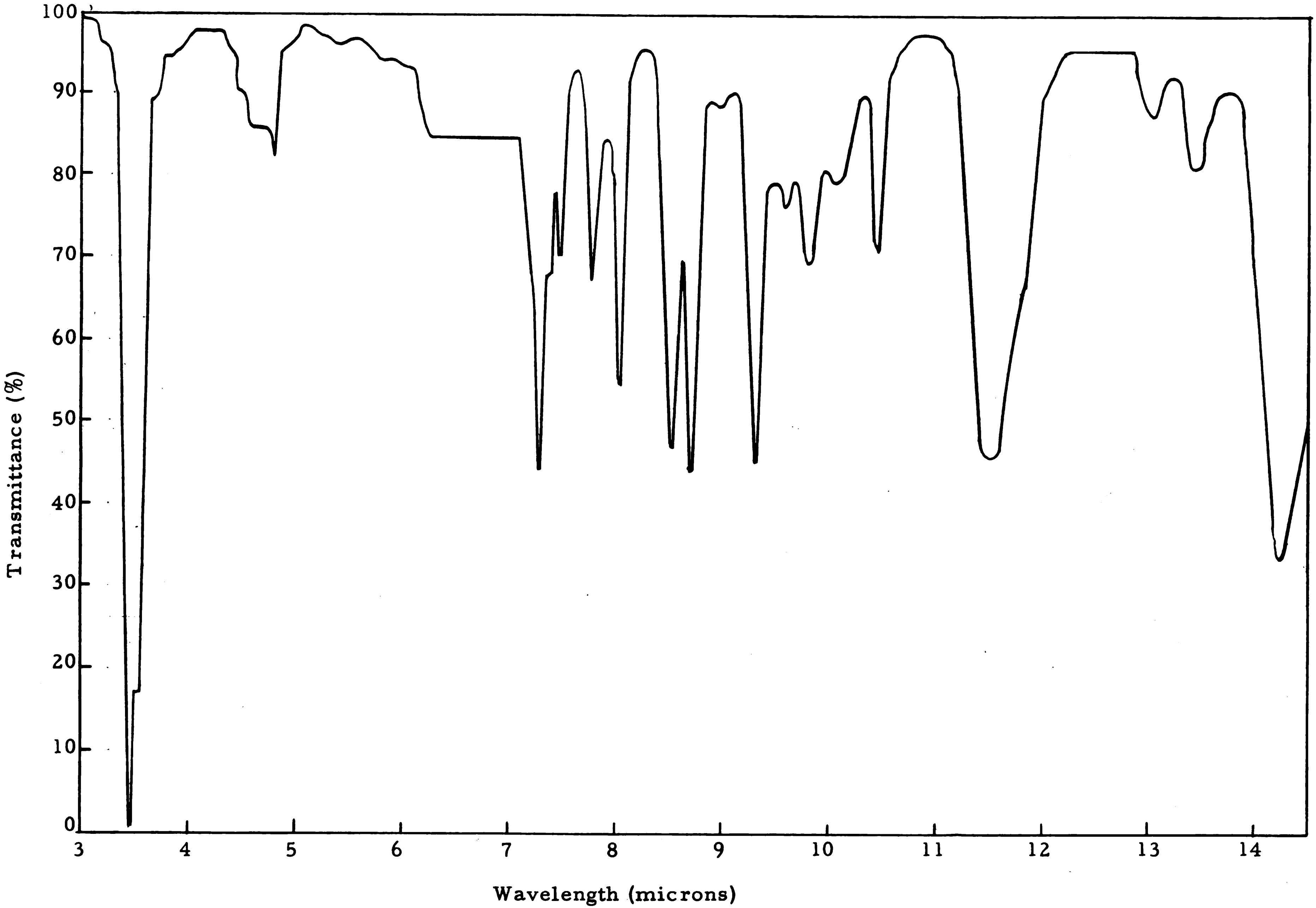
Infrared spectra of ϕ_3SnCl in carbon disulfide.



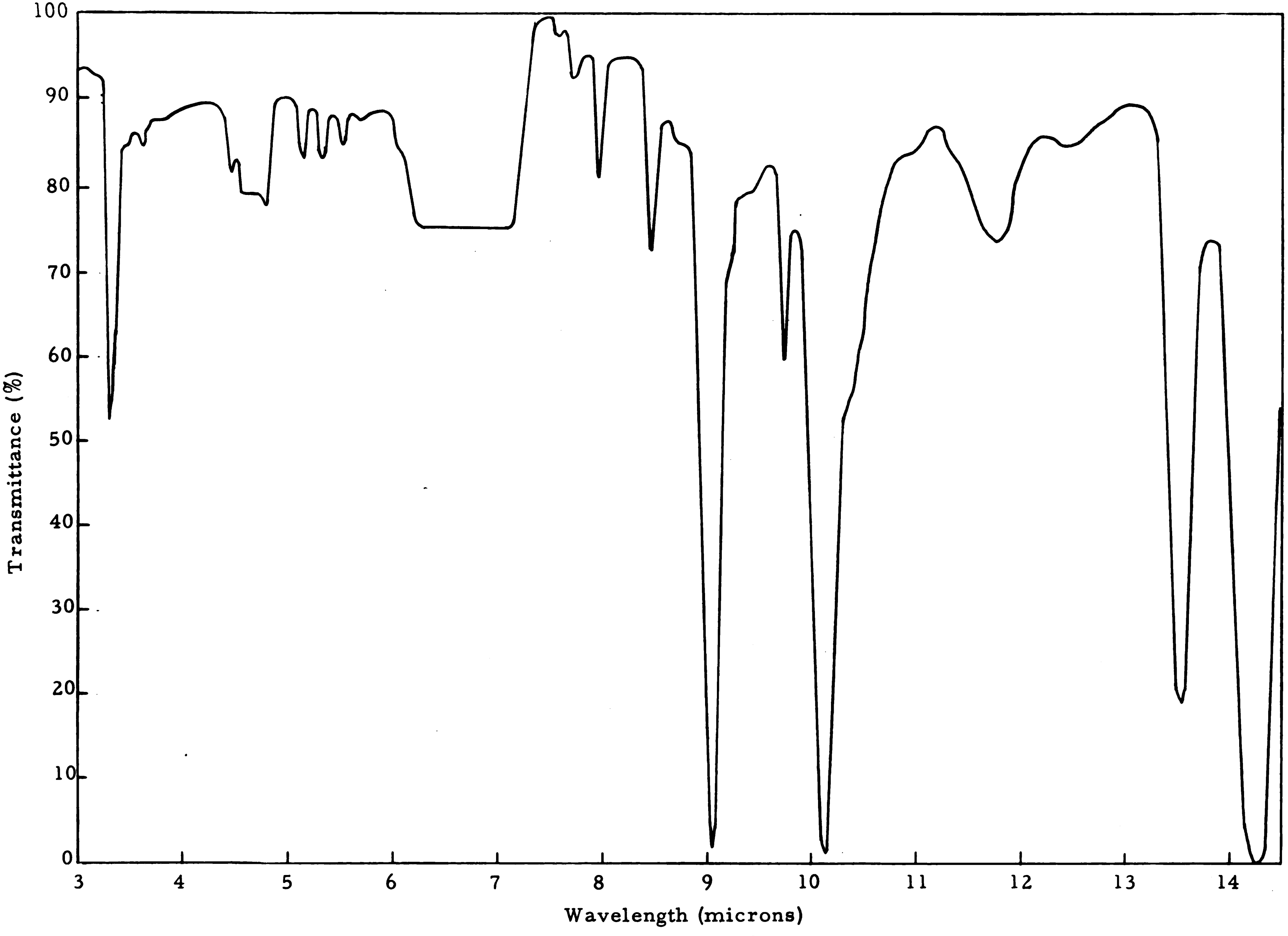
Infrared spectra of ϕ_2SnCl_2 in carbon disulfide.



Infrared spectra of $(CH_3)_2SnCl_2$ in carbon disulfide.



Infrared spectra of $(\underline{n}\text{-}C_4H_9)_2SnCl_2$ in carbon disulfide.



Infrared spectra of NaOSiϕ_3 in carbon disulfide.

APPENDIX E

Sodium Chloride Rate Data

Run No.	Compound	Initial $NaOSi\phi_3$ conc. ($\underline{N}$)	Reaction time (min.)	Sodium chloride yield (%)
1	$\phi_3SiOSn\phi_3$	0.00783	2.1	95.3
2	$\phi_3SiOSn\phi_3$	0.00783	2.4	95.1
3	$\phi_3SiOSn\phi_3$	0.00783	5.6	95.9
4	$\phi_3SiOSn\phi_3$	0.00783	24.7	96.3
5	$\phi_3SiOSn\phi_3$	0.0127	1.1	96.2
6	$\phi_3SiOSn\phi_3$	0.0127	51.3	99.6
7	$\phi_3SiOSn\phi_3$	0.0127	2796.0	98.0
8	$\phi_3SiOSn\phi_3$	0.0134	0.9	93.4
9	$\phi_3SiOSn\phi_3$	0.0134	5.4	94.3
10	$\phi_3SiOSn\phi_3$	0.0134	1447.0	94.9
11	$\phi_3SiOSn\phi_3$	0.0299	0.8	96.3
12	$\phi_3SiOSn\phi_3$	0.0299	0.8	96.3
13	$\phi_3SiOSn\phi_3$	0.0299	5.6	96.8
14	$\phi_3SiOSn\phi_3$	0.0299	9.3	97.0
15	$\phi_3SiOSn\phi_3$	0.0299	27.5	97.2
16	$\phi_3SiOSn\phi_3$	0.0345	0.9	96.0
17	$\phi_3SiOSn\phi_3$	0.0345	27.8	97.4
18	$\phi_3SiOSn\phi_3$	0.0345	2994.0	97.6
18a	$\phi_3SiOSn\phi_3$	0.0490	0.8	94.2
19	$\phi_3SiOSn\phi_3$	0.0490	54.7	95.2
20	$\phi_3SiOSn\phi_3$	0.0490	2225.0	94.7
22	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0127	54.3	97.6
23	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0127	2978.0	98.0
25	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0134	54.5	94.6
26	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0134	8878.0	95.6
27	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	4.0	95.2
28	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	9.0	100.9
29	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	148.1	99.8
30	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0147	1207.0	99.7
31	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.026	1.1	95.8
32	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.026	44.8	96.8
33	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.026	2153.0	96.7

Continued

Run No.	Compound	Initial $NaOSi\phi_3$ conc. ($\underline{N}$)	Reaction time (min.)	Sodium chloride yield (%)
34	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	0.6	97.2
35	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	0.9	97.5
36	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	28.1	98.1
37	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0354	165.0	98.8
38	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0490	0.8	94.6
39	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0490	50.4	95.1
40	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0490	1560.0	94.9
41	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	1.1	96.8
42	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	7.0	97.3
43	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	21.5	97.9
44	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0492	65.4	98.3
45	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	0.6	97.2
46	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	10.3	98.2
47	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	41.8	98.2
48	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0302	853.0	98.4
49	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	0.7	92.6
50	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	14.7	96.7
51	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	64.4	96.6
52	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0359	352.0	96.9
53	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0430*	0.9	96.4
54	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0430	10.1	97.4
55	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0430	43.6	97.6
56	$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.0430	825.0	98.8
58	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0127	85.4	97.8
61	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0134	58.8	95.4
63	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	3.8	98.4
64	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	12.5	99.0
65	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	61.8	98.6
66	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0136	682.0	90.9
67	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0260	0.9	96.4
68	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0260	54.6	96.9
69	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0260	2795.0	97.2

Continued

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*Initial $(\underline{n}\text{-}C_4H_9)_2SnCl_2$ conc. is 0.0463 g. equiv./l.

Run No.	Compound	Initial $NaOSi\phi_3$ conc. (*N*)	Reaction time (min.)	Sodium chloride yield (%)
70	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0299	0.9	98.7
71	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0299	1.3	98.4
72	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0299	29.5	99.2
73	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0345	0.9	97.9
74	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0345	87.9	98.9
76	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0490	1.0	95.0
77	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0490	50.2	95.5
78	$(CH_3)_2Sn(OSi\phi_3)_2$	0.0490	2190.0	94.7