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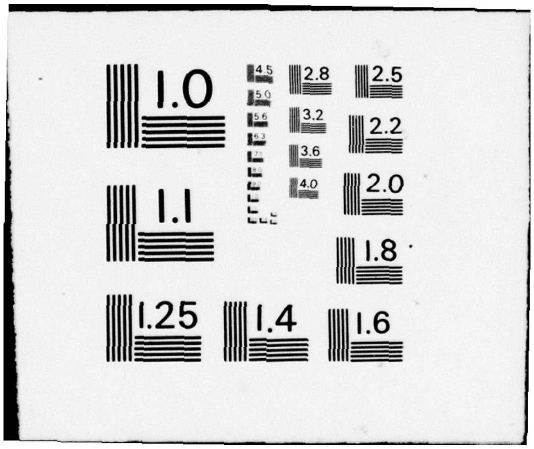
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Contract N00014-75-C-1024

Technical Report No. 76-1

ORGANOSILANE POLYMERS

by

J.P. Wesson and T.C. Williams

UNION CARBIDE CORPORATION

Tarrytown, New York 10591

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JAN 6 1977
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submitted to

DEPARTMENT OF THE NAVY

Office of Naval Research

Arlington, Virginia 22217

DECEMBER 1976

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(14) **REPORT DOCUMENTATION PAGE**		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TR-76-1 ✓	2. GOVT ACCESSION NO. -----	3. RECIPIENT'S CATALOG NUMBER -----
4. TITLE (and Subtitle) (6) ORGANOSILANE POLYMERS ✓		5. TYPE OF REPORT & PERIOD COVERED (9) Interim. Technical Tech. Report.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) (10) J. P. Wesson ~~and~~ T. C. Williams		8. CONTRACT OR GRANT NUMBER(s) (15) N00014-75-C-1024 NEW
9. PERFORMING ORGANIZATION NAME AND ADDRESS Union Carbide Corporation Tarrytown, New York 10591 ✓		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ------------
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA		12. REPORT DATE (11) Dec~~ember~~ 1976
		13. NUMBER OF PAGES 35 (12) 38p.
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) ----------------		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Technical Report Distribution List

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

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18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silanes
Polysilanes
Organopolysilanes

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Purified dialkyldichlorosilane monomers were reacted with alkali metals in organic solvent solutions to form linear diorganosilane homopolymers and copolymers. The organosilane polymers were characterized by spectrometric and thermal analysis. Polymer solubilities in organic solvents were determined. Formation of polymer charge transfer complexes were briefly examined.

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INTRODUCTION

Background

The first preparations of polydimethyl silanes as reported by Burkhard were heterogeneous materials made up of benzene soluble lower polymers, insoluble probably cross-linked polymers and fractions containing appreciable amounts of oxygen probably as silanol and siloxane (11). Formation of polydimethyl silanes as impure byproducts from synthesis of permethylcyclosilanes have been noted by several workers (12). Investigations by H. Gilman, R. West, A. Allred and their coworkers established that catenated organosilicon chains possess unusual electronic qualities which in some aspects resemble those of conjugated carbon chains (13).

Recently, S. Yajima and coworkers have reported on the pyrolysis of dodecamethylcyclohexasilane $(Me_2Si)_6$ to form polycarbosilane oligomers which can be further pyrolyzed to form microcrystalline beta-silicon carbide fibers (14).

Objectives

The main objectives of this project are:

1. to prepare and generally characterize linear high molecular weight polydiorganosilanes;
2. *to investigate electroconductive properties of the polysilanes* and their charge transfer complexes;
3. to examine the behavior of selected cyclic and linear polydiorganosilanes under pyrolytic conditions.

Scope

This report covers initial work in the areas of monomer purification, chlorosilane polymerization and copolymerization, polysilane characterizations, and charge transfer complex formation in the period from May 1975 to June 1976.

I. MONOMERS

A. Background

This work section is concerned with preparation of silane monomers containing the lowest practicable concentrations of impurities that can interfere with linearity in the target polymers. The most readily available source of the dimethylsilylene ($-Me_2Si-$) chain unit is dimethyl dichlorosilane, Me_2SiCl_2. As it is ordinarily produced, industrial grade Me_2SiCl_2 contains small but significant amounts of other chlorosilanes (Table I) which can produce chain termination or branching in the target polymers. Impurity chlorosilanes such as $SiCl_4$ and Me_3SiCl can be brought to very low concentrations by careful fractional distillation. However, $MeSiCl_3$ which boils only 4°C below Me_2SiCl_2 cannot be reduced below about 10^{-2} mole % by ordinary distillation techniques. Polysilanes of any substantial degree of condensation are largely insoluble and cross-linked when produced from Me_2SiCl_2 containing $MeSiCl_3$ at this level. We therefore examined various purification procedures with the goal of providing Me_2SiCl_2 or an equivalent source of $-Me_2Si-$ with impurity levels of 10^{-3} mole % or less.

B. Analytical Methods

Gas chromatography was used to determine $MeSiCl_3$ content of Me_2SiCl_2. Effective separation of $MeSiCl_3$ was achieved using a DCLSC liquid phase (1) (50% trifluoropropyl, 1% vinyl, methyl silicone). Four types of detection methods have been examined.

1. Ordinary thermal conductivity detection is useful to 10^{-2} mole-%. By running at above normal filament temperatures detection at 10^{-3} mole-% is possible, but with drastically reduced filament life. Nevertheless, this method is useful where limited numbers of analyses are desired.

2. Flame ionization methods show similar detection limits of 10^{-2} - 10^{-3} mole-%, but are complicated by inordinate sensitivities to traces of hydrocarbons. This makes clean separation of the $MeSiCl_3$ peak difficult. Overall, this method was not considered promising.

3. Electron capture detection is extremely sensitive and appears capable of detecting $MeSiCl_3$ at 10^{-4} and possibly 10^{-5} mole-%. However, the method is non-linear in response to $MeSiCl_3$ and requires further study to develop a reliable calibration. Overloading of the detector by the main Me_2SiCl_2 component has also been a problem. Upon recovery the detector may not return to its initial sensitivity.

4. Mass spectrographic methods positively identified various impurities contained in Me_2SiCl_2. The $MeSiCl_3$ impurity was identified as the last material eluted before Me_2SiCl_2 on a 30% DCLSX chromatographic column. Other trace impurities were: Me_2SiF_2, and three branched heptanes. Simultaneous detection by flame ionization indicated that the $MeSiCl_3$ concentration was about 2×10^{-2} mole %. Similarly, analyses of impurities in comonomers, discussed later, were carried out.

C. Me_2SiCl_2 Purification

Plant grade Me_2SiCl_2 contains 2×10^{-2} to 9×10^{-2} mole % $MeSiCl_3$, typically 3×10^{-2} mole %. Reduction of this impurity to levels below 10^{-2} % were attempted by various methods.

1. Simple Distillation

Careful fractional distillation thru a variety of packing materials, i. e., nichrome helipac or lime glass beads, afforded a final cut (about 20% yield) of Me_2SiCl_2 containing typically 1.0 - 1.5 x 10^{-2} mole % $MeSiCl_3$.

2. Acetoxylation

The boiling point relationship of the methylacetoxysilanes differs from that of the methylchlorosilanes in several respects. As shown in Table I, the acetoxy silanes boil considerably higher than the corresponding chlorosilanes, the boiling points decrease monotonically as methyl substitution increases and the boiling point differences between members is large.

The following scheme was examined to separate $MeSiCl_3$ and Me_2SiCl_2:

(a) $\equiv SiCl + Ac_2O \longrightarrow \equiv SiOAc + \underset{\text{b.p. } 51°C}{AcCl}$

(b) Separation of $Me_2Si(OAc)_2$ from $MeSi(OAc)_3$ by fractional distillation

(c) $Me_2Si(OAc)_2 \xrightarrow[\text{1. } PCl_5 \text{ 2. } O_3]{} Me_2SiCl_2 + AcCl + \underset{\text{b.p. } 105.3°C}{POCl_3}$

Acetoxylation (a) proceeded smoothly and a single fractional distillation (b) reduced the trifunctional content to about 0.02 mole % but conversion of the acetoxysilane to chlorosilane with PCl_5 (C-1) was complicated by the appearance of PCl_3 in the system possibly from thermal decomposition, $PCl_5 \longrightarrow PCl_3 + Cl_2$. Since PCl_3 (b. p. 76°C) is very difficult to separate from Me_2SiCl_2, ozonation was used to convert it to $POCl_3$. All but a trace of PCl_3 was converted to $POCl_3$ but even repeated ozonations were unsuccessful in attacking this recalcitrant portion.

An alternate method of conversion from acetoxy- to chlorosilane has been devised in which less than stoichiometric amounts of thionyl chloride are reacted as in

$$Me_2Si(OAc)_2 + 2\,SOCl_2 \xrightarrow{\text{catalyst}} Me_2SiCl_2 + 2\,AcCl + 2\,SO_2$$

with tertiary alkyl phosphine or amine catalysts; this reaction proceeds nearly to completion at ambient temperatures in a few minutes. When less than stoichiometric proportions of $SOCl_2$ are used, further heating at reflux for one hour reduces residual $SOCl_2$ to undetectable levels. This method gave Me_2SiCl_2 containing approximately the same amount of $MeSiCl_3$ as the starting Me_2SiCl_2 used to prepare $Me_2Si(OAc)_2$. The $Me_2Si(OAc)_2$ was distilled at reduced pressure to minimize thermal elimination of acetic anhydride by the reaction:

$$2 \equiv SiOAc \longrightarrow \equiv Si - O - Si\equiv + Ac_2O$$

Apparently separation of $MeSi(OAc)_2$ was not achieved under these conditions. Success in purification of Me_2SiCl_2 by other means led to termination of this effort.

3. Via $(Me_2SiO_{3,4})$

In the industrial preparation of the high molecular weight dimethylsiloxane polymers which are the basis of silicone elastomers, trifunctional silicon compounds are removed by hydrolysis and condensation of the crude Me_2SiCl_2 to form a mixture of siloxane oligomers which are then subjected to a catalyzed siloxane rearrangement at elevated temperature and reduced pressure. Once low boiling components have been taken over, the rearranging mass forms cyclic dimethylsiloxanes, chiefly trimer and tetramer, which are continuously distilled over while the higher boiling branched material containing the trifunctional silicon units remains behind. The cyclic siloxanes produced in this way normally contain trifunctional silicon at the 10^{-3} mole % level or less. Thus, if a scheme could be devised for converting the cyclosiloxanes back to Me_2SiCl_2, it was expected that monomer at the desired purity level would result.

Thionyl chloride in the presence of basic nitrile, phosphine or amine catalysts is known to cleave dimethylcyclosiloxanes by reductive halogenation to form linear chloro terminated siloxane oligomers, e. g.

$$(Me_2SiO)_4 + SOCl_2 \longrightarrow Cl(Me_2SiO)_3Me_2SiCl + SO_2$$

and formation of small amounts of Me_2SiCl_2 with prolonged reaction times have been noted (2). It was therefore decided to look for more potent catalysts that would not only produce ring opening but also promote further attack on the linear oligomers.

In considering this approach, it was also necessary to deal with the problem of separating Me_2SiCl_2 and unreacted $SOCl_2$ since these materials boil only 8.7°C apart. It was decided to use a high boiling carboxylic acid to decompose unreacted $SOCl_2$ according to

$$R\overset{O}{\overset{\|}{C}}OH + SOCl_2 \longrightarrow R\overset{O}{\overset{\|}{C}}Cl + HCl \quad + \quad SO_2$$

and adipic acid was chosen for initial trials. This produced an unexpected but desirable intensification of reaction as described later.

Nine candidate catalysts including hexamethylphosphoric triamide (HMPA), triethylphosphine, and ferric chloride were screened. Those listed produced 51.3, 22.0 and 64.8 mole % yields of Me_2SiCl_2 respectively under roughly comparable conditions. With HMPA or $FeCl_3$ catalysts, the reaction appears to proceed as in

$$(Me_2SiO)_4 + 3\,SOCl_2 \longrightarrow 2\,Me_2SiCl_2 + (ClMe_2Si)_2O + 3\,SO_2$$

and beyond this stage slows considerably probably because the disiloxane $(ClMe_2Si)_2O$ is more resistant to attack.

Where unreacted $SOCl_2$ was present, distillation produced Me_2SiCl_2 containing appreciable amounts of contaminating $SOCl_2$ as anticipated. When adipic acid was added to a $FeCl_3$ catalyzed reaction mixture before distillation, residual $SOCl_2$ was rapidly destroyed and surprisingly the contained yield of Me_2SiCl_2 rose from 51.6 mole % to 64.8 mole %.

G.C. analysis indicated heavy contamination of Me_2SiCl_2 even after fractional distillation. Contamination prevented determination of $MeSiCl_3$ content. This approach was dropped when success was achieved by other methods.

4. By Partial Hydrolysis

Since $MeSiCl_3$, the impurity of main concern in Me_2SiCl_2, hydrolyzes considerably faster than Me_2SiCl_2 to form higher boiling methylchlorosiloxanes, the slow partial hydrolysis of impure Me_2SiCl_2 followed by distillation to isolate unreacted Me_2SiCl_2 was examined. This approach afforded a reduction in $MeSiCl_3$ from about 0.9 mole % to 0.12 — 0.06 mole % with a yield of 68% in first trials. Extensive trials were then run at temperatures ranging from -50° to 70°C. While reductions of $MeSiCl_3$ to the $1\text{-}2 \times 10^{-2}$ mole % level were achieved, reductions below this level were not obtained. This method has been abandoned.

5. Via $(Me_2Si)_6$

Purified $(Me_2Si)_6$ was converted to Me_2SiCl_2 by the reaction

$$(Me_2Si)_6 + 6\,SO_2Cl_2 \xrightarrow[\text{pyridine}]{} 6\,Me_2SiCl_2 + 6\,SO_2$$

However, chlorination of methyl groups also occurred to the extent of about 1-2% making this reaction unsuitable.

6. Et_2O Codistillations

Careful codistillation of Me_2SiCl_2, containing 200-300 ppm $MeSiCl_3$, with Et_2O through a 45 cm lime glass bead column yielded a fraction (c. 20%) of Me_2SiCl_2 containing about 20 ppm $MeSiCl_3$.

Further experiments have been run with diethyl ether under different reflux and distillation schedules to probe the nature of the separation process. The most plausible mechanism appears to be slow ether cleavage (probably by traces of HCl that are inevitably present), formation of a silane ethoxy ester and subsequent redistribution of the ethoxy group between the silane species present. This can be represented as:

$$Et_2O \xrightarrow{HCl} EtCl + EtOH \xrightleftharpoons{Me_2SiCl_2} \underset{(1)}{MeSiCl(OEt)} \xrightleftharpoons{MeSiCl_3} \underset{(2)}{MeSiCl_2(OEt)}$$

After reflux with diethyl ether, plant grade Me_2SiCl_2 was found to contain traces of the esters 1, 2. Reflux of Me_2SiCl_2 with 2-3% $Me_2Si(OEt)_2$ yielded similar results in reducing $MeSiCl_3$ levels.

This method has allowed purification of Me_2SiCl_2 initially containing 300 ppm $MeSiCl_3$ to yield Me_2SiCl_2 with 10-20 ppm $MeSiCl_3$ in sufficient quantities to satisfy project needs.

D. Other Monomers

1. The following purchased chlorosilane monomers (Petrarch) were fractionally distilled:

a. $EtMeSiCl_2$
b. $Me(n\text{-}Pr)SiCl_2$

The $MeSiCl_3$ content of $EtMeSiCl_2$ was found to be about 70 ppm. $MeSiCl_3$ was not detected in the other monomers. Impurity identification of these monomers is in progress using g. c. - mass spectroscopic methods.

2. $t\text{-}BuMeSiCl_2$

Preparation of $t\text{-}BuMeSiCl_2$ by reaction of t-BuLi and $MeSiCl_3$ resulted in crude products containing silanic hydride (SiH) probably by side reactions of the type:

$$MeSiCl_3 + t\text{-}BuLi \longrightarrow MeSiHCl_2 + Me_2C{=}CH_2 + LiCl$$

Reactions of this sort have been reported (3). Distilled yields of $t\text{-}BuMeSiCl_2$ were low (10-30%) with yields of accompanying SiH containing material running typically at 50-60%. Further work will attempt to reduce side reactions and improve yields.

3. $Cl(Me_2Si)_6Cl$ and $Me(Me_2Si)_6Cl$

The compounds $Cl(Me_2Si)_6Cl$ and $Me(Me_2Si)_6Cl$ were prepared by methods reported in the literature (4,5) by the following reactions:

$$(Me_2Si)_6 + PCl_5 \xrightarrow[Cl_2HCCHCl_2]{} \underset{(27\%)}{Cl(Me_2Si)_6Cl}$$

$$Cl(Me_2Si)_6Cl + MeMgBr \xrightarrow[Et_2O]{} \underset{(60\%)}{Me(Me_2Si)_6Cl}$$

These compounds were purified by fractional distillation and analyzed by g. c.

4. $Me_2Si(OEt)_2$ and $Me_2Si(OBu)_2$

The dimethyldialkoxy silanes were prepared by vacuum esterification of Me_2SiCl_2 with the appropriate alcohol followed by addition of the appropriate sodium alkoxide to drive the reaction to near completion.

$$Me_2SiCl_2 + ROH \xrightarrow[\substack{Et_2O \\ NaOR}]{-HCl} Me_2Si(OR)_2$$

The silane esters were purified by fractional distillations. These compounds were used in probing the mechanism of purification of the $Me_2SiCl_2\text{-}Et_2O$ distillation.

5. $Me_2Si(NR_2)_2$

Various dimethyl alkylaminosilanes (NR_2 = dimethyl amino, dipropylamino, piperidyl, morpholino) were prepared by addition of excess amine to a Me_2SiCl_2 solution at -30° :

$$Me_2SiCl_2 \xrightarrow[pentane\ -30^\circ]{HNR_2(excess)} Me_2Si(NR_2)_2 + R_2\overset{+}{N}H_2\overset{-}{Cl}$$

The amine hydrochloride byproduct was removed by filtration and the dimethylalkylaminosilane was purified by fractional distillation. These compounds were used in probing the mechanism of purification of the Me_2SiCl_2-Et_2O distillation.

6. Me_2SiBr_2 Via $(Me_2Si)_6$

Cleavage of the cyclic hexasilane $(Me_2Si)_6$ with bromine was examined briefly as an approach to high purity Me_2SiBr_2 at $Br_2/(Me_2Si)_6$ mole ratios from 10 to 1 at room temperatures from -45° C to +30° C and at reflux in n-hexane. In all instances a mixture of α, w-dibromosilanes was formed. The reaction was complicated by a side reaction of bromine with the solvent apparently catalyzed by U. V. from laboratory fluoroescent lights. Further trials with less susceptible solvents such as CBr_4 and CF_2Br_2 were deferred.

E. Experimental

1. $Me_2SiCl_2/MeSiCl_3$ Analysis

Gas chromatography was performed using a Hewlett-Packard 5734A gas chromatograph fitted with a 1/8" O. D. x 20 ft column. The column packing was 30% DCLSX on chromasorb W. Operating conditions were as follows:

Injection temperature - 200° C
Detector temperature - 200° C
Oven temperature - 50° C + 8° min^{-1} (to 180° C)
T. C. Detector current - 175 ma
Carrier gas - 30 psi He
Flow rate - 20 cc - min^{-1}
Attenuation - X 1

Using these conditions the smallest concentration of $MeSiCl_3$ which could be measured was about 10 ppm. The area of the $MeSiCl_3$ peak was calibrated vs. prepared $MeSiCl_3$ standards. Retention times for components of Me_2SiCl_2 samples are reported as follows:

Hydrocarbon	9 min
Hydrocarbon	10 min
Hydrocarbon	11 min
$MeSiCl_3$	12. 5 min
Me_2SiCl_2	13. 0 min

2. Dimethyldiacetoxysilane

In a 1000 ml flask equipped with a teflon stirbar, 18" helipac filled heated distillation column, stillhead, and N_2 inlet, combine 302 ml Me_2SiCl_2 (2. 5 mole) and 566 ml acetic anhydride (6. 0 mole). With the column heater off, reflux the reaction mixture overnight. Distill off the acetyl chloride slowly until the boiling point of the distillate reaches 75° C. About 335 ml of distillate will be collected. Set up the apparatus for vacuum distillation and turn on the column heaters. Distill at 150 mm-Hg pressure. The initial cut to 119° C was discarded. Collect a cut of $Me_2Si(OAc)_2$ boiling at 119° C at 150 mm. Yield: 153 g (34.8%).

3. Chlorination of $Me_2Si(OAc)_2$ with PCl_5

685 g PCl_5 (3.3 mole) is placed in a 1000 ml flask equipped with a 250 ml addition funnel, reflux condenser and N_2 inlet. 232 g $Me_2Si(OAc)_2$ (1.32 mole) is added dropwise. After the addition is complete the reaction mixture is refluxed for 6 hrs. The solution is distilled through a 45 cm helipac column and a cut boiling 65-75° C is collected containing Me_2SiCl_2 and PCl_3.

This solution is transferred to a 200 ml 3-neck flask equipped with a dry ice condenser and subnatant gas inlet tube. The solution is chilled to -50° C and a stream of O_3 in O_2 from a Welsbach O_3 generator is passed thru the solution until the blue O_3 color persists. O_3 generation is shut off and when the blue color vanishes the O_2 gas stream is shut off.

The solution is warmed to room temperature then distilled thru a 24" helipac column. A fraction is collected with the b. p. 70.2° C. G. C. shows this fraction contains about 1% PCl_3, and about 0.2% AcCl.

A second ozonation followed by distillation reduces the PCl_3 level to about 0.1%.

4. Chlorination of $Me_2Si(OAc)_2$ with Cl_2SO

To a solution of 125 ml $Me_2Si(OAc)_2$ (0.75 mole) and 4 ml Bu_3P: in a 250 ml flask equipped with an addition funnel and a reflux condenser with N_2 inlet, add 97 ml Cl_2SO (1.35 mole) dropwise. After the addition is complete reflux 1 hr. Distill the reaction mixture at a rate of about 20 $ml\text{-}hr^{-1}$ thru a 24" helipac column. Discard the AcCl and the transition cut until the stillhead temperature stabilizes at 70.1° C. A cut is taken at 70.1° C.

The distilled product contained $MeSiCl_3$ in quantities similar to unpurified Me_2SiCl_2 (100-200 ppm).

5. Chlorination of $(Me_2SiO)_4$ with Cl_2SO

In a 200 ml flask equipped with addition funnel and reflux condenser with N_2 inlet is placed 77 ml $(Me_2SiO)_4$ (0.25 mole), 4.0 g $FeCl_3$ and 3.0 g adipic acid. 65 ml Cl_2SO (0.90 mole) is added dropwise with stirring. The solution is then refluxed 3 hrs. After 3 hrs. the reaction is about 70% complete as shown by g. c. 1.5 g addition adipic acid is added and reflux continued 1.5 hr. The mixture is distilled thru a 24" helipac column. The first 10 ml is discarded. A fraction of about 21 g (18%) of Me_2SiCl_2 is collected at 70.4° C. Analysis (g. c.) of the pot residue showed additional Me_2SiCl_2 in the undistilled reaction mixture.

Analysis (g. c.) showed the $MeSiCl_3$ content to be significantly greater than in starting Me_2SiCl_2 (200-300 ppm) at the time of this experiment. The analytical methods had not been developed to the point where accurate values could be assigned to $MeSiCl_3$ concentrations.

A similar reaction was run using 22 ml hexamethyl phosphoramide in place of the $FeCl_3$-adipic acid catalyst. A yield of 56 g of Me_2SiCl_2 (43%) was collected. $MeSiCl_3$ analysis was not possible on this sample due to contamination by a number of unknown materials with retention times similar to $MeSiCl_3$ and Me_2SiCl_2.

6. Chlorination of $(Me_2Si)_6$ with Cl_2SO_2

In a 50 ml flask equipped with addition funnel and a reflux condenser with N_2 inlet is placed 7.0 g $(Me_2Si)_6$ (0.02 mole). 16 ml Cl_2SO_2 (0.20 mole) is added dropwise. The reaction mass refluxed rapidly. Upon cooling the reaction is heated at reflux for 17 hrs and cooled. 0.2 g pyridine is added to decompose residual Cl_2SO_2 and the solution refluxed for 30 min. The mixture is fractionated through a 12" glass helix column. After a short forerun, a fraction 1.9 g (12%) is collected b. p. 70.0°C. This material was heavily contaminated by materials boiling close to Me_2SiCl_2 and $MeSiCl_3$ analysis could not be carried out.

7. Me_2SiCl_2 Purification by Partial Hydrolysis

302 ml Me_2SiCl_2 (2.5 mole) in a 500 ml flask equipped with a mechanical stirrer, reflux condenser with N_2 inlet and addition funnel is cooled to 0°C. With rapid stirring 13.5 ml H_2O (0.75 mole) (30% hydrolysis) is added dropwise over 2 hrs. Me_2SiCl_2 is stripped out of the solution under vacuum at 0°C using a dry ice -propanol bath to cool the receiving flask. The Me_2SiCl_2 is fractionated through a 12" helipac column. The first 20 ml is discarded and 119 g (37%) of Me_2SiCl_2 collected.

Similar reactions were run from -40°C to +70°C with 15 to 30% hydrolysis. Dioxane and ethylene glycol were used as carrier solvents for the H_2O.

All experiments showed $MeSiCl_3$ levels similar to or greater (about 2X) than those of unpurified Me_2SiCl_2 (about 200 ppm).

8. Me_2SiCl_2 - Et_2O Codistillations

A mixture of 190 ml Me_2SiCl_2 (300 ppm $MeSiCl_3$) and 100 ml Et_2O is distilled through a 45 cm lime glass bead column at a rate of about 25 ml-hr^{-1}. The Et_2O (35°C) and transition (35-70.0°C) cuts are discarded and three fractions collected. The $MeSiCl_3$ levels as analyzed by g. c. are:

Cut	B. P. (°C)	Yield	$MeSiCl_3$ (ppm)
1	70.0 - 70.2	43 g (22%)	138 ppm
2	70.2	39 g (22%)	60 ppm
3	70.2	43 g (24%)	18 ppm

Similar results have been observed for codistillations using 20% Et_2O or 4% $Me_2Si(OEt)_2$.

Similar distillations without a source of the (EtO-) group have never produced a cut of Me_2SiCl_2 containing less than 90-100 ppm $MeSiCl_3$.

9. $EtMeSiCl_2$

200 g $EtMeSiCl_2$ (Petrarch) is distilled thru a 45 cm glass bead packed column under N_2. The distillation is run at total reflux for 30 min until the head temperature stabilizes at 75°C. Distillate is collected at a rate of 30 $ml\text{-}hr^{-1}$ and a transition cut boiling over the range 75-100°C collected until the still head temperature stabilizes at 100.0°C. A cut of $EtMeSiCl_2$ is collected at 100.0°C, yield 106g (53%).

Analysis by g.c. indicates a $MeSiCl_3$ content of 70 ppm.

10. Me n-$PrSiCl_2$

200 g Me n-$PrSiCl_2$ (Petrarch) is distilled thru a 45 cm glass bead packed column under N_2. The distillation is run at total reflux for 1 hr until the still head temperature stabilizes at 115°C. Distillate is collected at a rate of 50 $ml\text{-}hr^{-1}$, and a transition cut is collected over the range 115-125°C until the still head temperature stabilizes at 125.0°C. A cut of $MePrSiCl_2$ is collected at 125.0 - 125.5°C, yield 115g (58%).

Gas chromatography showed this sample to contain less than 100 ppm $MeSiCl_3$ or $MeHSiCl_2$ although an absolute determination could not be done at the time the distillation was run.

11. t-Bu $MeSiCl_2$

In a two liter flask equipped with mechanical stirrer, addition funnel and reflux condenser with N_2 inlet is placed 350 ml $MeSiCl_3$ (3.0 mole). 2.0 mole t-BuLi in 850 ml n-pentane (Ventron) is added dropwise with stirring over 2 hrs. The rate of addition is adjusted to maintain a mild reflux. The solution is allowed to stand overnight, then vacuum filtered under N_2 to remove LiCl. The solution is fractionally distilled thru a 45 cm column filled with beryl saddles to remove n-pentane, unreacted $MeSiCl_3$ and all components boiling to 120°C. After cooling, the pot residue is transferred to a 250 ml flask. The reaction mixture is then distilled through a 20 cm heated Vigreaux column and a heated still head to prevent solidification of the product. A transition cut boiling, 115-134°C, is discarded. A cut with the boiling range 134-7°C is collected, yield 79g (23%).

Analysis by g.c. showed considerable impurities, among those present were t-$BuHSiCl_2$. Purity was 96%.

Redistillation thru a heated 30 cm nichrome ring filled column gave a product with 99.0% purity.

Analysis of the pot residue of the above reaction showed about a 60% yield of higher boiling materials containing considerable SiH.

12. $Cl(Me_2Si)_6Cl$ (4)

Using a procedure described by Gilman and Inoue (4), 71 g $(Me_2Si)_6$ (0.20 mole) dissolved in 300 ml 1,1,2,2-tetrachloroethane is placed in a 1000 ml flask equipped with a magnetic stir bar and a reflux condenser with N_2 inlet. 56 g PCl_5 (0.26 mole) is added to the flask and the mixture heated rapdily to reflux. The solution is refluxed nine minutes, then cooled. The solvent and volatile fractions are stripped off using a rotary evaporator. The oily residue was then distilled thru a heated 12" Vigreaux column at about 1 mm-Hg. A cut collected between 60-120°C is discarded, then solid unreacted $(Me_2Si)_6$ begins to build up in the still head. The reaction is shut down, the still head washed out with pentane, and a heating tape applied to the still head to prevent solidification of products. The cut boiling from about 140-165°C is discarded. A cut with the boiling range 165-174°C is collected, yield 27 g (32%).

This product was shown to be 99.2% pure by g.c. containing about 0.8% unreacted $(Me_2Si)_6$.

13. $Me(Me_2Si)_6Cl$ (5)

This material is prepared by a modification of procedure reported by Boberski and Allred (5). A solution of 18.5 g $Cl(Me_2Si)_6Cl$ in 100 ml anhydrous Et_2O is put into a 200 ml flame dried flask equipped with subambient thermometer, reflux condenser and addition funnel. The solution is chilled to 0°C and 0.04 moles of CH_3MgI in 14 ml Et_2O added dropwise with stirring over 1 hour. The solution is stirred for 30 min at 0°C then refluxed for 30 min. The solution is evaporated in a rotary evaporator. The oily solid is taken up in 100 ml hexane, gravity filtered and evaporated to yield a clear oil. The oil is distilled through a 12" Vigreaux column at about 1 mm-Hg. A cut boiling 145-172°C is collected. Yield 8.98g.

Gas chromatography showed this material to be 63.3% $Me(Me_2Si)_6Cl$, 21.1% $Me(Me_2Si)_6Me$, and 12.4% $(Me_2Si)_6$. The material was used with no further attempt to purify it.

14. $Me_2Si(OEt)_2$

In a 250 ml flask equipped with an addition funnel and a reflux condenser with N_2 inlet is placed 121 ml Me_2SiCl_2 (1.0 mole). 129 ml EtOH (2.2 mole) is added dropwise over 30 min. The solution is refluxed 3 hours. A solution of 0.05 mole EtONa in 60 ml EtOH is added and the solution stirred overnight. Additional 0.025 mole EtONa is added in 30 ml EtOH and the solution stirred 3 hours. The mixture is then fractionally distilled through a 45 cm column filled with Raschig rings. A cut of $Me_2Si(OEt)_2$, b.p. 113.0-113.5°C is collected. Yield 23.4 g (16%).

G.C. showed this product to be 99.6% pure containing 0.4% $(Me_2SiCl(OEt)$.

15. $Me_2Si(OBu)_2$

A procedure similar to that for $Me_2Si(OEt)_2$ was followed using 151 ml Me_2SiCl_2 and 263 ml 1-butanol. The product was distilled thru a Vigreaux column at 40 mm-Hg pressure b. p. 103-106° C, then redistilled through a 12" glass bead column at 100 mm-Hg. A fraction is collected boiling at 118. 5-119. 5° C, yield 106 g (59%).

The product was 98. 1% pure containing 1. 9% $Me_2SiCl(OBu)$.

16. $Me_2Si(NMe_2)_2$

In a 2000 ml flask equipped with mechanical stirrer and N_2 inlet a solution of 315 g Me_2NH (7. 0 mole) in 1000 ml n-pentane is cooled to -40° C. 152 ml Me_2SiCl_2 (1. 25 mole) is added dropwise with stirring, the mixture stirred at -30° C for 30 min following addition, then allowed to warm to ambient temperature slowly. The dimethyl ammonium chloride is removed by vacuum filtration under N_2. The filtered solid is washed with 1000 ml fresh pentane. The solutions are combined and evaporated to yield a yellow oil which is fractionally distilled through a 45 cm glass bead filled column b. p. 127. 5° -128° C, yield 81 g (44%).

G. C. showed this material to be 99+% pure.

17. $Me_2Si(NPr_2)_2$

Using a similar procedure as described for $Me_2Si(NMe_2)_2$, 70 ml Me_2SiCl_2, and 410 ml Pr_2NH in 400 ml pentane gave 63 (42%) $Me_2Si(NPr_2)_2$, b. p. 160-3° C at 60 mm-Hg in 99+% purity.

18. $Me_2Si(Piperidyl)_2$

Using a similar procedure as described for $Me_2Si(NMe_2)_2$, 70 ml Me_2SiCl_2 and 295 ml piperidine ~~gave~~ IN 400 ml pentane yielded 42 g $Me_2Si(Piperidyl)_2$, b. p. 153° C at 40 mm-Hg in 97% purity.

19. $Me_2Si(Morpholino)_2$

Using a similar procedure as described for $Me_2Si(NMe_2)_2$, 70 ml Me_2SiCl_2 and 261 ml morpholine in 400 ml pentane gave 29 g of $Me_2Si(Morpholino)_2$ b. p. 149-150° C at 20 mm-Hg in 94% purity.

II. POLYMERIZATIONS

A. $(Me_2Si)_6$

$(Me_2Si)_6$ was prepared by a number of published methods (6, 7). The preferred method was cyclization of Me_2SiCl_2 with NaK in THF which was reported to us by West and Wojnowski (8). This method gave $(Me_2Si)_6$ in 58% yield and 99. 8+% purity.

B. $(EtMe_2Si)_6$

Reaction of $EtMeSiCl_2$ in dilute THF solution with excess NaK alloy yielded a distillable material believed to be the cyclic hexasilane in about 30% yield. Further analysis has shown this material to contain on the average one SiH and one $-SiCH_2Si-$ per molecule of cyclic.

The cyclic $(EtMeSi)_6$ has been prepared by rearrangement of $(EtMeSi)_x$ with K-napthalide. Further details will be discussed in future reports.

C. Permethylpolysilane Oligomers

Permethylpolysilane oligomers, $Me(Me_2Si)_nMe$, where n=12, 18, 24 were prepared by K (metal) coupling of $Me(Me_2Si)_6Cl$ and $Cl(Me_2Si)_6Cl$ in heptane by a modification of the procedure reported by Boberski and Allred (9). These oligomers were used as reference standards in thermal analysis and gel permeation chromatographic analysis experiments.

D. Alkali Metal Coupling of Me_2SiCl_2

1. Autogenous Pressure Reactions

The first reported preparations of polydimethylsilylenes employed coupling of dimethyldichlorosilane by reaction with molten sodium in benzene solvent (5). In order to retain monomer and solvent, both of which boil below the melting point of sodium at atmospheric pressure, the reaction was conducted in an autoclave under autogenous pressures.

This method was examined in several trials which employed Me_2SiCl_2, sodium and purified n-octane as solvent in 300 ml rocking autoclave. At 140°C, tan to white octane insoluble powders were obtained. Yields were not substantially increased by extended reaction times and were, for example, 58.7 mole % at 5 hours and 60.1 mole % after 29 hours.

At this point, no further work with this method is planned in view of the more convenient atmospheric pressure method described below.

2. Atmospheric Pressure Reactions

Me_2SiCl_2 was reacted with a freshly prepared Na dispersion in octane in a flame dried flask in a dry N_2 atmosphere. The reaction vessel is equipped with an efficient condenser since the reaction does not proceed until the melting point of Na is reached. Reflux for 24 hr yields a blue solid. The color has been shown to be caused by traces of excess Na in the by-product NaCl. The crude polymer was worked up by addition of ethanol: acetic acid followed by THF, EtOH, 10% aqueous $NaHCO_3$, and H_2O washes. Yields of the polymer are typically 70-90% containing less than 0.4% SiO.

E. Base Catalyzed Silane Rearrangements

1. Background

Carberry and West reported the rearrangement of crude polydimethylsilylenes catalyzed by sodium naphthalide in THF to give good yields of $(Me_2Si)_6$ (7). It is reasonable to assume that a ring-chain equilibrium is involved here with the ring form greatly favored by the presence of a good solvent. In absence of solvent, it is quite likely that the equilibrium will be shifted toward the chain form and the point of interest is whether that shift will be large enough to be useful in the formation of linear polymer.

2. Na/HMPA Catalyst

Some range finding experiments have been made to determine whether solutions of sodium in hexamethylphosphoric triamide (HMPA) would catalyze silane rearrangement and if so what problems might be encountered. Both crude polydimethylsilylene and $(Me_2Si)_6$ are essentially insoluble in HMPA alone but are rapidly dissolve in Na/HMPA solutions with a distinctive color change of the solution from blue to red. The red solution color is rapidly discharged to colorless or faint yellow by reagents such as methanol or water with evolution of a gas. After discharge with water, no ether soluble material could be found, indicating that the polysilane had been completely converted to water soluble material. When the red solution was discharged with methanol rather than water, a species believed to be $Me_2Si(OMe)_2$ was detectable in the reaction mixture. This suggests that water quenching may have formed silanolate salts,such as $Me_2Si(ONa)_2$, which are very water soluble. Further experiments along these lines suggest that methoxide ion formed in methanol quenching leads to extensive attack on Si-Si bonds and rapid conversion to methoxy silane esters. Thus, work-up procedures involving weaker bases may be needed. Experiments employing quenching agents such as $PhMe_2SiCl$ are in progress. Here it is expected that the weaker chloride ion will not attack the polysilane linkages so readily. Once a suitable technique has been developed, we will proceed to examine rearrangements under conditions which favor chain formation as much as possible.

3. Na Napthalide Catalyst

Reaction of $(Me_2Si)_6$ with a trace of Na-napthalide in THF, followed by removal of THF in vacuo and long equilibration of the solid before termination with H_2O yielded only $(Me_2Si)_6$ containing a trace of napthalene. These results seem to indicate either (a) rearrangement of $(Me_2Si)_x$ to $(Me_2Si)_6$ by a Na/Napthalide catalyst does not proceed by an equilibrium process or (b) if the rearrangement does occur by an equilibrium process the formation of cyclic is favored so strongly that the reverse reaction is not detectable.

F. Development of Effective Me_3Si- Chain Termination

Initial experiments in Na coupling in refluxing octane of Me_2SiCl_2 containing 4-20 mole-% of Me_3SiCl showed that the chain terminating monomer was not coupling efficiently. Low yields of CCl_4 and cyclohexane soluble polymers with molecular weights of 600-1500 (estimated by nmr) were isolated and DTA examination of the higher polymer fraction showed a decrease in melting endotherms from 390°C to about 300°C.

The reaction of Me_3SiCl with Na in refluxing octane gives poor yields ($< 5\%$) of $Me_3SiSiMe_3$. By contrast the use of K or NaK gives 80% or greater yield of $Me_3SiSiMe_3$. Effective incorporation of Me_3Si was achieved by use of NaK or K in place of Na metal in the polymerization reaction.

A series of polymers have been prepared using Me_2SiCl_2 containing 2, 4, 8, 12.5 and 20 mole % Me_3SiCl with NaK alloy and n-hexane. Evaluation by D.S.C. indicates that as the % Me_3SiCl used increases, the characteristics of the polymer change indicating that some modification of the final polymer is occurring.

When the solution properties of these endblocked polymers were measured in perhydrofluorene at 2% concentration, the following observations were made:

1. Polydimethylsilane prepared without endblocker dissolves around 220°C and precipitates around 211°C.

2. As the concentration of endblocker used increases from 2 to 20%, the temperature at which the polymer was completely dissolved decreased to 205°C. The polymers appeared to dissolve slowly as temperature increased starting at about 155° - 160°C. Dissolving of polymer prepared without endblocker occurred at much higher temperatures over the range 215 - 225°C. This suggests that as endblocker concentration increases, the polydispersity of molecular weight distribution in the polymer increases. Solubility properties are discussed further under Characterization.

3. The SiO content of the polymers produced was in the range of 0.5-0.7%.

It was concluded that the Me_3SiCl was being incorporated into the polymer. Quantitative measurements of the effectiveness of Me_3SiCl endblocking will be made pending development of a method for molecular weight determination.

G. EtMeSi/Me_2Si Copolymers

Copolymerizations of mixtures of Me_2SiCl_2 and $EtMeSiCl_2$ by Na(metal) coupling in n-octane produced polysilanes which were shown to contain -EtMeSi- units by I-R analysis. Copolymer compositions are given in Table II. Further characterization by I-R indicated the presence of SiH in these compounds. The tendency of +EtMeSi+ units to form SiH is presently being examined and will be discussed in a future report. Percent SiO was typically less than 0.8%.

H. MePrSi/Me_2Si Copolymers

Copolymerizations of mixtures of Me_2SiCl_2 and Me n-PrSiCl_2 by Na(metal) coupling in n-octane produced polysilanes which were shown to contain Me n-PrSi units by I. R. Reaction mixtures containing greater than 30 mole % Me n-PrSiCl_2 yielded only soluble products, in other words, no precipitated polymer was recovered from the reaction mixture. Development of methods to work up these soluble products is in progress and will be discussed in a future report.

I. Experimental

1. $(Me_2Si)_6$ (8)

In a flame dried 5000 ml flask equipped with a mechanical stirrer, addition funnel, and reflux condenser with N_2 inlet, 92 g Na, 500 g K, and 3200 ml of fresh THF were refluxed with stirring until a homogenous NaK alloy formed. The suspension was cooled, and 970 ml Me_2SiCl_2 was added dropwise over 6 hrs at a rate so that reflux was maintained. The reaction mixture was refluxed for 24 hrs. The solution was cooled and 100 ml 50% aqueous acetic acid was added dropwise with stirring, carefully, to consume excess NaK alloy. After addition the mixture which now was a blue paste was split into two portions and each portion was poured into a 4000 ml beaker. 1000 ml H_2O was added to each portion. The organic layer of each portion was set aside. The aqueous solutions were combined and were extracted with 3 x 1000 ml n-pentane. The pentane extracts were combined with the organic solutions from above, and the combined solution was washed with 2000 ml cold H_2O. The organic solution was evaporated to yield a solid which was dissolved in 1000 ml n-pentane and filtered to remove polymer. The solution was evaporated to yield 379 g (82%) of crude product.

The crude $(Me_2Si)_6$ was recrystallized from hot 360 ml THF + 2840 ml - 95% ethanol. The crystals were collected by vacuum filtration, washed with 200 ml cold methanol and dried in vacuum. Yield: 247 g.

The recrystallization solution was evaporated to yield a white solid which was recrystallized from 60 ml THF + 400 ml 95% EtOH. Yield: 59 g.

The $(Me_2Si)_6$ was then combined and recrystallized from hot 300 ml THF + 2400 ml 95% ethanol. The product was collected by vacuum filtration and dried in vacuo. Yield: 268 g (58%).

This product was analyzed by IR, NMR, and g. c. and was shown to be 99. 8+% pure.

2. $Me(Me_2Si)_nMe$; n = 12, 18, 24 (9)

In a 200 ml flame dried flask equipped with mechanical stirrer and reflux condenser with N_2 inlet were put 5. 7 g ($Me(Me_2Si)_6Cl$) and 5. 96 g $Cl(Me_2Si)_6Cl$ in 100 ml heptane, and 1. 7 g K. The solution was refluxed with stirring 18 hours, then cooled, and 0. 012 moles MeMgI in 4. 0 ml Et_2O was added. The solution was refluxed for 30 min. then cooled. A solution of 40 ml 50% aqueous acetic acid was added dropwise with stirring. The mixture was poured into a 500 ml separatory funnel, 100 ml hexane was added and the organic suspension was washed with 200 ml 10% aqueous $NaHCO_3$, followed by 2 x 250 ml H_2O. The organic layer was then evaporated to yield a white solid.

The white solid was extracted with 200 ml hot hexane and the suspension filtered. The solid was set aside (A). The hexane solution was chilled in ice to 5° C and stirred over 10 ml conc. H_2SO_4 for 20 min. The hexane solution was decanted, washed with 4 x 200 ml H_2O, filtered thru $CaSO_4$ and evaporated to yield a white solid.

The white solid was stirred in 150 ml hot ethanol and was filtered hot. The solid ($Me(Me_2Si)_{18}Me$) was set aside. The solution was concentrated to yield a solid which was recrystallized twice from 30 ml hot ethanol to yield 0.29 g (2.9%) of $Me(Me_2Si)_{12}Me$. The material was characterized by IR, and DSC (mp 150°).

The crude $Me(Me_2Si)_{18}Me$ was recrystallized from hot 100 ml hexane + 100 ml ethanol. The solid was collected by filtration. Yield: 0.25 g of $Me(Me_2Si)_{18}Me$ identified by IR and DSC (mp 197°).

The solid set aside above (A) was stirred in 100 ml hot CCl_4 and filtered. The solution was cooled and 200 ml ethanol was added. The white precipitate was collected by filtration. The crude $Me(Me_2Si)_{24}Me$ was dissolved in 20 ml hot CCl_4 and 20 ml ethanol was added. The precipitated $Me(Me_2Si)_{24}Me$ was collected by filtration and was dried in vacuo. Yield: 0.26 g of $Me(Me_2Si)_{24}Me$ identified by IR and DSC (mp 218°).

The insoluble polymer was set aside and dried. Yield: 2.71 g.

3. $\underline{-\!\!(Me_2Si)\!\!-_x}$

In a flame dried 250 ml flask equipped with addition funnel, mechanical stirrer, and reflux condenser with dry N_2 inlet reflux 11.5 g Na (0.50 mole) in 110 ml n-octane for 15 min and cool. Add 20.2 ml Me_2SiCl_2 and reflux for 18-24 hrs. Cool the mixture and add 50 ml acetic acid + 50 ml ethanol dropwise and stir 1 hr. Collect the solid by vacuum filtration. Wash the solid with 200 ml THF, followed by 200 ml ethanol. The organic solution and wash is set aside.

The blue solid collected above is then agitated in a Waring blender successively with 300 ml H_2O, 300 ml 10% aqueous $NaHCO_3$, then 300 ml H_2O. The flocculant white precipitate is collected by vacuum filtration, and dried in vacuo over P_2O_5 for at least 2 days. Typical yield: 11.6 g (80%) of a fine white solid containing less than 0.5% SiO.

The organic solution above is extracted with 300 ml H_2O, 300 ml 10% aqueous $NaHCO_3$ and 300 ml H_2O. The organic solution was filtered thru $CaSO_4$ and evaporated to yield silanic oils which were shown by IR and g.c. to be a complex mixture of (Me_2Si) and (Me_2SiO) units.

4. (Me_3Si) endblocked $(Me_2Si)_x$

Using the reaction mixtures given in the table below, (Me_3Si)- endblocked -$(Me_2Si)_x$ was prepared using the procedure reported for $(Me_2Si)_x$.

(% Me_3Si)	Me_2SiCl_2	Me_3SiCl	Na	K	n-Hexane
2	23.9 ml	0.5 ml	3.7 g	9.4 g	100 ml
4	23.7 ml	1.0 ml	3.7 g	9.4 g	100 ml
8	23.2 ml	2.1 ml	3.7 g	9.4 g	100 ml
12.5	22.6 ml	3.4 ml	3.7 g	9.4 g	100 ml
20.0	21.5 ml	5.6 ml	3.7 g	9.4 g	100 ml

Yields of precipitated $(Me_2Si)_x$ ranged from 70% to about 40% as the Me_3Si content increased. These materials were examined by IR and DSC and will be discussed further under characterization.

Soluble dimethyl silane oligomers were collected from the organic solutions and were also characterized as above.

5. EtMeSi-Me_2Si Copolymers

Using the reaction mixtures given in the table below various (EtMeSi-Me_2Si) copolymers were prepared using the procedure discussed for $(Me_2Si)_x$.

% (EtMeSi)	Me_2SiCl_2	$EtMeSiCl_2$	Na	Octane
0	30.2 ml	---	11.5 g	110 ml
10	27.2 ml	3.4 ml	11.5 g	110 ml
30	21.2 ml	10.2 ml	11.5 g	110 ml
50	15.2 ml	17.0 ml	11.5 g	110 ml
80	6.0 ml	27.0 ml	11.5 g	110 ml
100	---	33.8 ml	11.5 g	110 ml

The products were worked up in a manner similar to $(Me_2Si)_x$ and the white solids were characterized by IR, DSC, and solubility.

III. CHARACTERIZATIONS

A. Infrared Spectroscopy

Polysilane samples were characterized as KBr wafers by infrared spectroscopy. The SiO content of polysilanes was determined using the 1035-1040 cm^{-1} absorption bond which is characteristic of the SiO moiety. The best polysilane samples prepared contained less than 0.5% SiO (dimethyl silicone = 100%).

Infrared absorption spectra of the EtMeSi/Me_2Si copolymers displayed bands at 1455, 1020, and 945 cm^{-1} attributed to the EtMeSi moiety. Concentrations of -EtMeSi- units in the copolymers were calculated using the relative intensities of the 945 cm^{-1} absorption band (Table II).

The presence of SiH in some polysilanes was detected by a fairly strong absorption band around 2100 cm^{-1}. Further investigations to determine the source of the SiH are in progress.

B. Solubility of $(Me_2Si)_x$ and $(EtMeSi/Me_2Si)_x$

The homopolymer $(Me_2Si)_x$, not surprisingly, was found to be insoluble in common solvents at ambient temperatures.

Various high boiling solvents were screened at 2 wt % conc. of $(Me_2Si)_x$ to determine at what temperature the polymer would dissolve. A list of these solvents is given in Table III. Results are generally accurate to ± 5°C.

The best solvent found, perhydrofluorene, dissolves as much as 8 wt % $(Me_2Si)_x$ at temperatures approaching the boiling point (253°C).

For polymers incorporating Me_3Si-endblocker, it was found that as the Me_3SiCl content of the starting monomer charge increased, the solution temperatures decreased as shown below:

$(SiMe_2)_x$ prepared using NaK in n-Hexane, perhydrofluorene solvent

Me_3SiCl Endblocker (mole %)	Solution Temp. (°C, 2% wt polymer)	Precipitation Temp. (°C, 2% wt polymer)
0	220	211
2	211	204
4	211	206
8	209	205
12.5	206	196
20.0	205	193

The incorporation of (EtMeSi) units into $(Me_2Si)_x$ drastically lowers the temperature at which the copolymer dissolves as shown in Figure 1. Apparently, the presence of -EtMeSi- units interferes with crystallization of the polymer and increases solubility. Where workable solution temperatures have been achieved, molecular weight determinations are planned. This work will be described in a future report.

C. Thermal Analysis

1. Permethylpolysilane Oligomers

DSC and TGA traces for the silane oligomers, $Me(Me_2Si)_nMe$ n=12, 18, 24 display characteristic endotherms (Figure 2):

a. an endotherm around 75-100°C attributed to a structural transition (not shown in Figure 2),

b. a fairly sharp endotherm around the known melting points of each compound,

c. a broad endotherm region which corresponds to the region of rapid weight loss observed by TGA. This endotherm is attributed to pyrolytic decomposition of the linear oligomer to cyclics and other volatile species.

2. Permethyl Polysilanes

The insoluble higher molecular weight polymer from the oligosilane synthesis, $Me(Me_2Si)_{6n}Me$, and polydimethyl silane, $(Me_2Si)_x$, were also examined by DSC and TGA. These DSC curves are also included in Figure 2. The following conclusions have been reached from this set of DSC curves:

a. the lower broad endotherm for each sample probably corresponds to the melting range of each sample. Weight loss by TGA is minimal over this temperature range. The position of this endotherm indicates that the higher oligosilane, $Me(Me_2Si)_{6n}Me$ contains fractions with greater than 24 silicon atom per chain; the broadness of the curve indicates a substantial molecular weight distribution is present.

The lower endotherm of the polydimethylsilane sample, indicates that this material is of considerably higher molecular weight than both the $Me(Me_2Si)_{24}Me$ and $Me(Me_2Si)_{6n}Me$ samples.

b. The upper endotherm is associated with a rapid weight loss observed by TGA. This weight loss does not occur to any great extent until melting of the polymer has occurred indicating that the pyrolysis is dependent upon temperature and the physical state of the polymer.

3. Me_3Si Endblocked Polysilanes

DSC and TGA traces for Me_3Si- endblocked polysilanes exhibit characteristic endotherms (Figure 3):

a. The DSC curve for $(Me_2Si)_x$ (0% Me_3Si-) prepared from NaK is essentially the same as $(Me_2Si)_x$ prepared using Na metal.

b. As the (Me_3Si) content increases from 2% to 8% there is a broadening of the lower (melting) endotherm indicating that the molecular weight distribution is broadened toward lower molecular weight. At 8% Me_3Si, the demarcation between the two endotherms is barely perceptible.

c. From 8% to 20% Me_3Si- the two endotherms overlap and appear as one and the lower limits of the endotherm broaden downward. These phenomena indicate that broadening of the molecular weight distribution occurs toward lower molecular weights and that the pyrolysis reaction of the polymer occurs within the melting range. The fact that rapid weight loss, recorded by TGA, begins at about 380° (0% Me_3Si-) and moves steadily downward toward 300° as the Me_3Si- content approaches 20% supports this inference.

It was concluded that Me_3Si- was incorporated into the polymer causing lowering of average molecular weight and broadening of the molecular weight distribution.

4. EtMeSi-Me_2Si Copolymers

DSC and TGA curves of the EtMeSi/Me_2Si copolymers exhibit characteristic endotherms (Figure 4).

a. As the EtMeSi content increases from 0 to 57% the characteristic melting and pyrolysis endotherms broaden but retain distinct identities.

b. Above 57% the endotherms overlap and lose their individual identities to become a single endotherm.

From DSC data alone it is not possible to conclude if EtMeSi units incorporated into the polymer are changing the physical properties of a polymer of similar molecular weight to $(Me_2Si)_x$ or if the EtMeSi units function as endblockers to lower molecular weight.

However, IR data indicates that EtMeSi is incorporated into the polymer at concentrations close to the $EtMeSiCl_2$ content of the starting monomer. This indicates that the reactivity of $EtMeSiCl_2$ is similar to that of Me_2SiCl_2. Based upon this evidence it is inferred that changes in the thermal characteristics of the polymer are due to a reduction of crystallinity, by EtMeSi units rather than any substantial reduction in average molecular weight.

D. NMR Spectra of Soluble Polydimethyl Silanes

Soluble polysilane fractions were separated from a polymerization of Me_2SiCl_2 containing 20% Me_3SiCl. The ratio of Me_3Si- units to -Me_2Si- units by ${}_1H^1$ NMR showed these fractions to contain average chain lengths of 13 and 17. These results agreed closely with estimates of molecular size from the melting curves estimated by DSC. It was concluded that NMR might be useful in determining molecular size for soluble samples.

E. Molding Tests

Molding tests in a positive pressure piston mold were made to obtain an initial estimate of the pressure-temperature conditions needed to produce fusion of the polymer powder and thermoplastic flow. Solid wafers were formed with the polydimethylsilylenes at 4,000 psi and temperatures of 235° to 285°C. The molded polymers were bluish-grey to white in color and quite brittle at room temperature. The polymer apparently has a large coefficient of expansion since it frequently cracks in the mold during cooling.

Further work using a KBr pellet mold indicates that polydimethylsilane can be molded at room temperature in vacuo ($P < 1mm$) at piston pressure ranging from 10,000 to 120,000 psi. Tests indicated that uniform samples were formed at 20,000 psi with no discernable further differences above that pressure. Polydimethylsilane molded in this manner produces white, brittle, slippery, waxy pellets, which fracture when cut. The density of these pellets was found to be $0.971 \pm .005$.

Pressure molding of EtMeSi / Me_2Si copolymers indicated that as the -EtMeSi- content increases to about 60% the samples become more pliable. This observation agrees with the concept of reduction of crystallinity by incorporation of bulky comonomer units. Above 60% EtMeSi content, the molded pellets become more brittle as the polymer approaches 100% EtMeSi homopolymer. Reduction of brittleness is indicative of reduction of crystallinity. Copolymers containing substantial amounts of both monomers are expected to be less crystalline than either homopolymer.

F. Gel Permeation Chromatography

An attempt was made to modify a gel permeation chromatograph (Waters Model 100) to permit molecular weight determinations of $(Me_2Si)_x$ at temperatures at which the polymer is soluble in dicyclohexyl (typically 220°C).

The fluid transport section was modified by:

1. Use of argon blankets at the inlet and outlet of systems.
2. Replacement of microstyrogel column packing with Dow Corning porous glass beads.
3. Replacement of teflon sealed sample injection valve with a polyimide sealed valve.
4. Doubling of oven heater wattage.

The modified instrument was capable of operation in the fluid transport section at 220-225° for extended periods.

Rapid deterioration of the CdS photocells of the refractive index detector at temperatures above 90°C was overcome by substitution of a silicon photodiode detector obtained from Waters. This detector is thermally stable to 150°C. Gas cooling of the detector was incorporated into the unit. The detector was optically attenuated to be twice as sensitive as the original detector to reduce background noise of the electronics. The detector could be maintained at 100°C with the fluid transport system at 160°C.

Experiments at 160° showed the system to be unacceptably noisy and the eluted solvent showed the presence of gas bubbles. It was determined that the optical cell had developed cracks due to thermal stress. Apparently, the optics were not designed to tolerate extreme temperatures.

Work in this area has been deferred since development of new optics would require resources beyond those of the present project definition.

G. Experimental

1. Infrared Spectroscopy

a. % SiO

Polysilane samples were prepared as KBr wafers using approximately 2-3 mg sample in 600 mg KBr.

The %SiO reference was prepared as follows: 0.2 mg diemthyl silicone oil in 0.2 ml benzene was added to 600 mg KBr. The benzene was evaporated and the KBr wafer was prepared. This reference represents 100% SiO.

Samples were run on a Bechman IR-12 spectrometer. The intensity of the absorption band around 1035-1040 cm^{-1} was used to calculate % SiO.

$$\%\ \text{SiO} = (\text{Abs.}_s \cdot \text{Wt}_r \, / \, \text{Abs.}_r \cdot \text{Wt}_s) \times 100$$

s = sample
r = reference

Samples in KBr safers were also used to measure the entire IR spectrum of polysilanes.

b. % EtMeSi

To determine the -EtMeSi- content of EtMeSi/Me_2Si copolymers, KBr pellets of the copolymers and pure $(\text{EtMeSi})_x$ homopolymer were prepared.

Three characteristic absorption bands occur for the EtMeSi moiety at 945 cm^{-1}, 1020 cm^{-1} and 1455 cm^{-1}. The -EtMeSi- content of each copolymer was calculated using the absorption of the band at 945 cm^{-1} with respect to the intensity of this band in the $(\text{EtMeSi})_x$ homopolymer.

c. SiH

The presence of SiH in some copolymers was detected by an absorption band at around 2100 cm^{-1}. In some cases, presence of SiH was also verified by NMR and wet chemical methods.

2. Solubility

Solubility of various polysilane samples was determined by preparing a suspension of 0.1 g sample in 4.9 g test solvent under a dry N_2 atmosphere. Dry N_2 was slowly bubbled through the liquid suspension. (When the test solvent was solid at room temperature, a solid mixture was used.) The suspension was transferred to a two-neck 5 ml flask equipped with subnatant 0-360°C thermometer and air cooled condenser with dry N_2 inlet. The suspensions were heated using a 25 ml heating mantle and sand heat transfer medium rapidly to 100°C, then at a heating rate of about 8°C min^{-1}. The suspension was heated with agitation and the temperature at which the polymer dissolved (if it dissolved) was recorded. The power to the heaters was then shut off and the temperature at which clouding persisted upon cooling was recorded.

The polysilane samples were recovered after cooling by dissolving the test solvent in an appropriate second solvent such as hexane and filtration of the resultant suspension.

3. DSC-TGA

DSC and TGA data were acquired using the following equipment:

Dupont DSC cell
Dupont 950 TGA analyzer
Dupont 990 thermoanalyzer programmer.

Polysilane samples were dried in vacuum oven P_2O_5 for at least 48 hrs before analysis.

Samples of 5.0 mg for DSC and approximately 8.0 mg for TGA were used. The samples were purged for 20 min. under a helium atmosphere. Both DSC and TGA were run at a rate of 10°C min^{-1} from ambient to 500°C under a helium atmosphere.

4. Pressure Molding

Approximately 0.5 g to 0.6 g of polysilane sample was loaded into a KBr pellet press with a piston area of 1.33 cm^2 (0.21 in^2). The mold was evacuated to pressure less than 1 mm Hg and the mold was pressed with forces over the range of 1 to 12 tons (9,500 - 114,000 psi) for 3 minutes using a hydraulic press. Pressure was maintained at the desired level as the sample slowly compressed.

The samples were pressed out of the mold and evaluated for physical properties.

IV. CHARGE TRANSFER (CT) COMPLEXES

A. CT Acceptors

TCNQ (Tetracyanoquinodimethane) was purified by recrystallization from CH_3CN followed by sublimation at reduced pressure.

TCNE (Tetracyanoethylene) was recrystallized from chlorobenzene and dried in vacuum.

B. CT Complexes

1. TCNE

C. T. complexes between TCNE and catenated silicon compound previously reported in the literature (10) were prepared as model systems.

C. T. complexes were then prepared between TCNE and two soluble $(Me_2Si)_x$ fractions. The product of reaction between the Si_{13} fraction mentioned previously in this report and TCNE in a 1:1 ratio exhibited an absorption shoulder in the near U. V.

A complex between TCNE and a distillable polydimethylsilane fraction containing linear silane fragments of 4 to 10 silicon atoms, plus a small amount of cyclic $(Me_2Si)_6$, was formed in approximately 1:1 ratio. This complex is interesting in that two U. V. absorption maxima are seen, one forming immediately and the second after about 180 seconds. Data for all of the complexes formed is given in the following table.

Polysilane - TCNE Complexes

Donor	Λ_{max}	ϵ_{max}
Me_6Si_2	406 nm	0.33 cm^{-1} M^{-1}
$(Me_2Si)_6$	505 nm	0.75 cm^{-1} M^{-1}
$(Me_2Si)_{13}$	387 nm (shoulder)	----
$(Me_2Si)_{4-10}$	431 nm 632 nm	0.85 cm^{-1} M^{-1} 0.20 cm^{-1} M^{-1}

Preparation of TCNE complexes of well characterized soluble polysilane fractions is in progress and will be described in a future report.

2. TCNQ

Attempts to detect C. T. complex formation between TCNQ and the four polysilane donors have been unsuccessful so far.

Further work in this area is planned and will be described in a future report.

C. Experimental

1. Polysilane - TCNE CT Complexes

In a typical preparation, 0.62 g $(Me_2Si)_6$ (1.8 m mole) and 0.23 g TCNE (1.8 m mole) were dissolved in 10 ml $CHCl_3$ which had been distilled and sparged with argon. The preparation was carried out in a dry N_2 atmosphere. The solution was stirred for 30 minutes, gravity filtered and a visible U.V. spectrum run from 700 nm to 300 nm on a Beckman DB-G U.V.-visible spectrophotometer. A 1 cm path length cell was used.

$$\Lambda_{max} = 505\ \text{nm};\quad \text{Abs}_{505} = 0.135;\quad \epsilon_{505} = 0.75\ \text{cm}^{-1}\ \text{M}^{-1}$$

V. ELECTRICAL CONDUCTIVITY

No work was performed in this area during the report period.

VI. WORK PLANNING JUNE, 1976 - MAY, 1977

A. Work will be continued with the copolymers:

$(Me_2Si/EtMeSi)$
$(Me_2Si/Me\ n\text{-}PrSi)$
$(Me_2Si/MePhSi)$

with respect to:

1. reducing SiH formation,
2. improved workup of reaction products,
3. molecular weight determination of soluble fractions.

B. Further investigation of cyclization reactions of comonomers will be made.

C. Film casting trials aimed at improving film quality will be carried out.

D. Pyrolyses reactions of copolymers and cyclization will be examined.

E. Formation of C.T. complexes of soluble silanes with TCNE or TCNQ will be attempted.

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TABLE I

BOILING POINTS OF SOME SILANE MONOMERS

	Boiling Points (°C, 760 mm Hg)		
X =	Cl-	Br-	CH_3CO_2-
SiX_4	57.6	153.	303.
CH_3SiX_3	66.1	133.	222.
$(CH_3)_2SiX_2$	70.1	112.	170.
$(CH_3)_3SiX$	57.7	80.	103

TABLE II

COPOLYMER COMPOSITION

$[(Me_2Si)_{100-y}(EtMeSi)_y]_x$

Charging Concentration [EtMeSiCl$_2$] (mole - %)	Copolymer Concentration (1) [EtMeSi] (y, mole - %)
0	0
10	10.8
20	20.0
30	31.7
45	44.1
60	57.2
80	88.2
100	100

TABLE III

Solvents for $(Me_2Si)_x$ (2 wt %)

	T_s (°C)	T_p (°C)
Perhydrofluorene	219	204
Acenapthene	216	209
Fluorene	220	219
Cyclodecane	229	213
Dicyclohexyl	232	214
1,5 Diazobicyclo [5.4.0] Undec-5-ene	240	222
Phenanthrene	250	244
10,11-Dihydro-5H-Dibenzocycloheptane	265	254
Bibenzyl	267	248
9,10 Dihydroanthracene	269	260
2,2-Diphenylpropane	272	260
trans-Stilbene	273	264
Xanthene	275	267
Diphenyl acetylene	277	268
Anthracene	278	271
4 (3-phenylpropyl) pyridine	280	275
9-Methyl anthracene	287	272
Triphenyl amine	288	282
4-azafluorene	289	278
Triphenyl methane	289	283
9-Cyano phenanthrene	289*	280*
Thioxanthene	290	275
Phenazine	292	281
Acridine	295	280
Phenanthridine	300	287
7,8-Benzoquinoline	300	275
5,6-Benzoquinoline	301	293
2,5-Diphenyloxazole	303	294
p-Terphenyl	304	296
Eicosane	332	318
Docosane	339	323

T_s - temperature at which 2 wt % $(Me_2Si)_x$ dissolved on heating

T_p - temperature at which 2 wt % $(Me_2Si)_x$ began to precipitate upon cooling

* - partial solubility

FIGURE 1: SOLUBILITY OF $((Me_2Si)_{100-b}(EtMeSi)_b)_x$ (2 wt.% in perhydrofluorene)

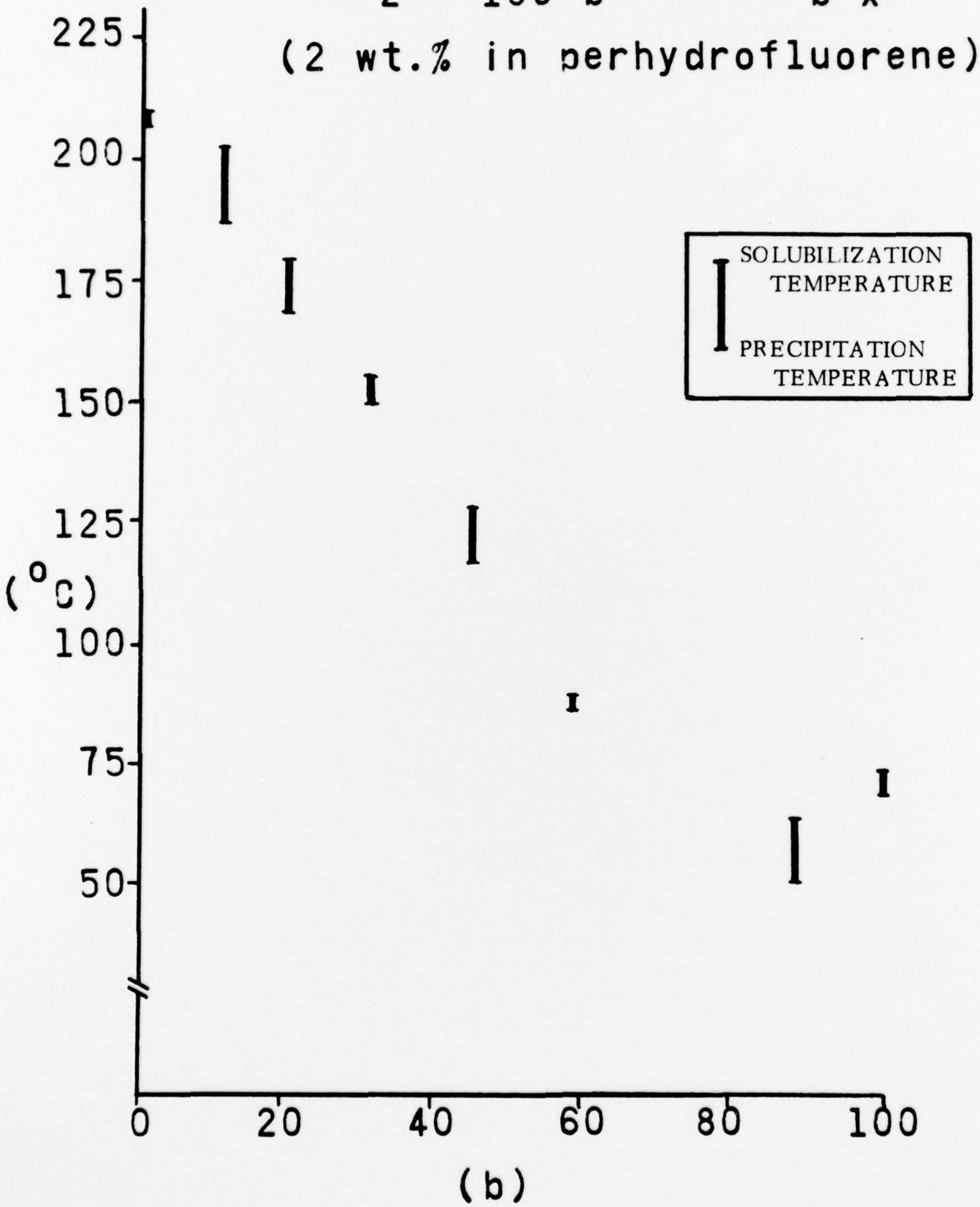

FIGURE 2: DIFFERENTIAL SCANNING CALORIMETRY OF POLYSILANES

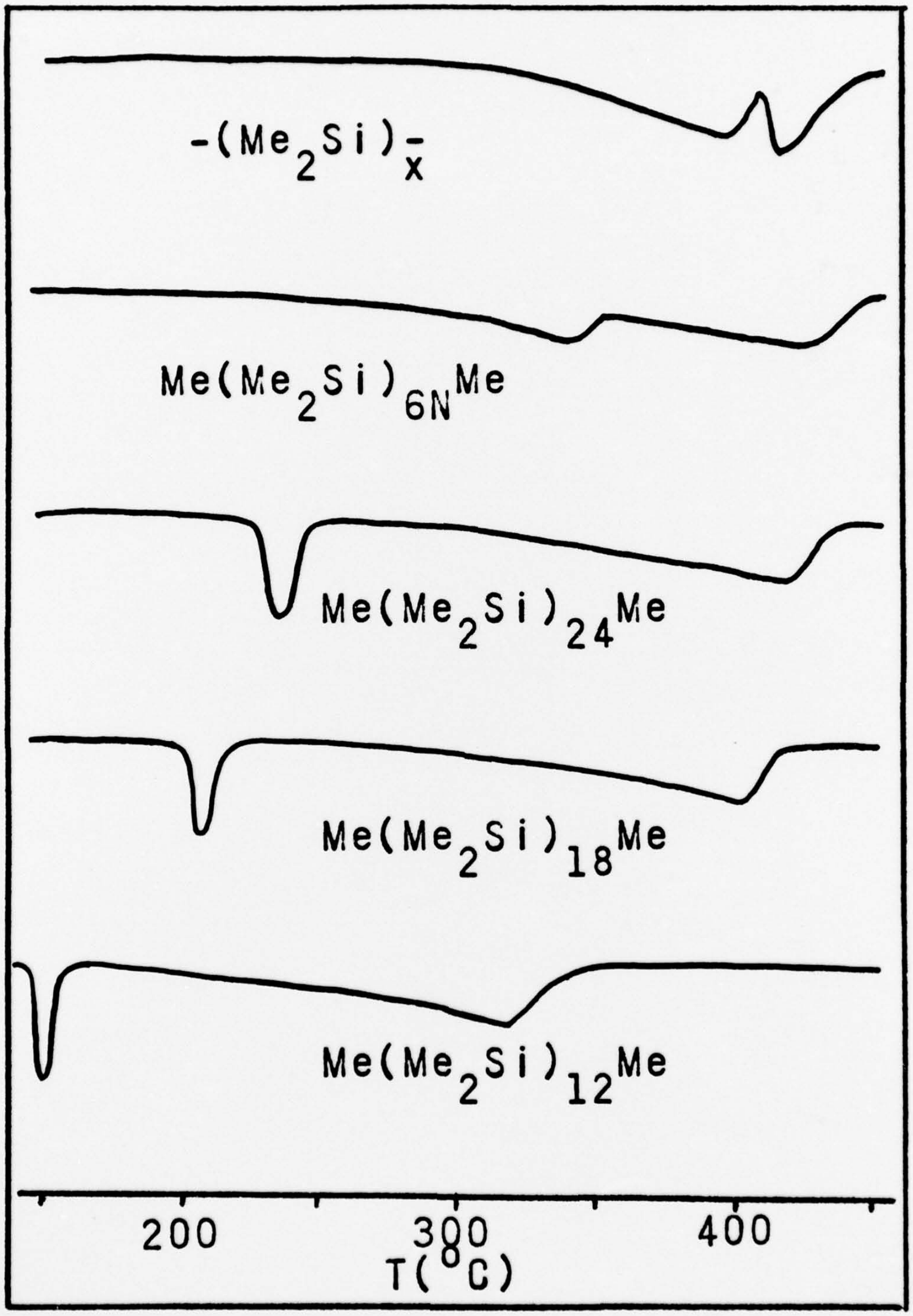

FIGURE 3: DIFFERENTIAL SCANNING CALORIMETRY OF Me_3Si-ENDBLOCKED POLYSILANES

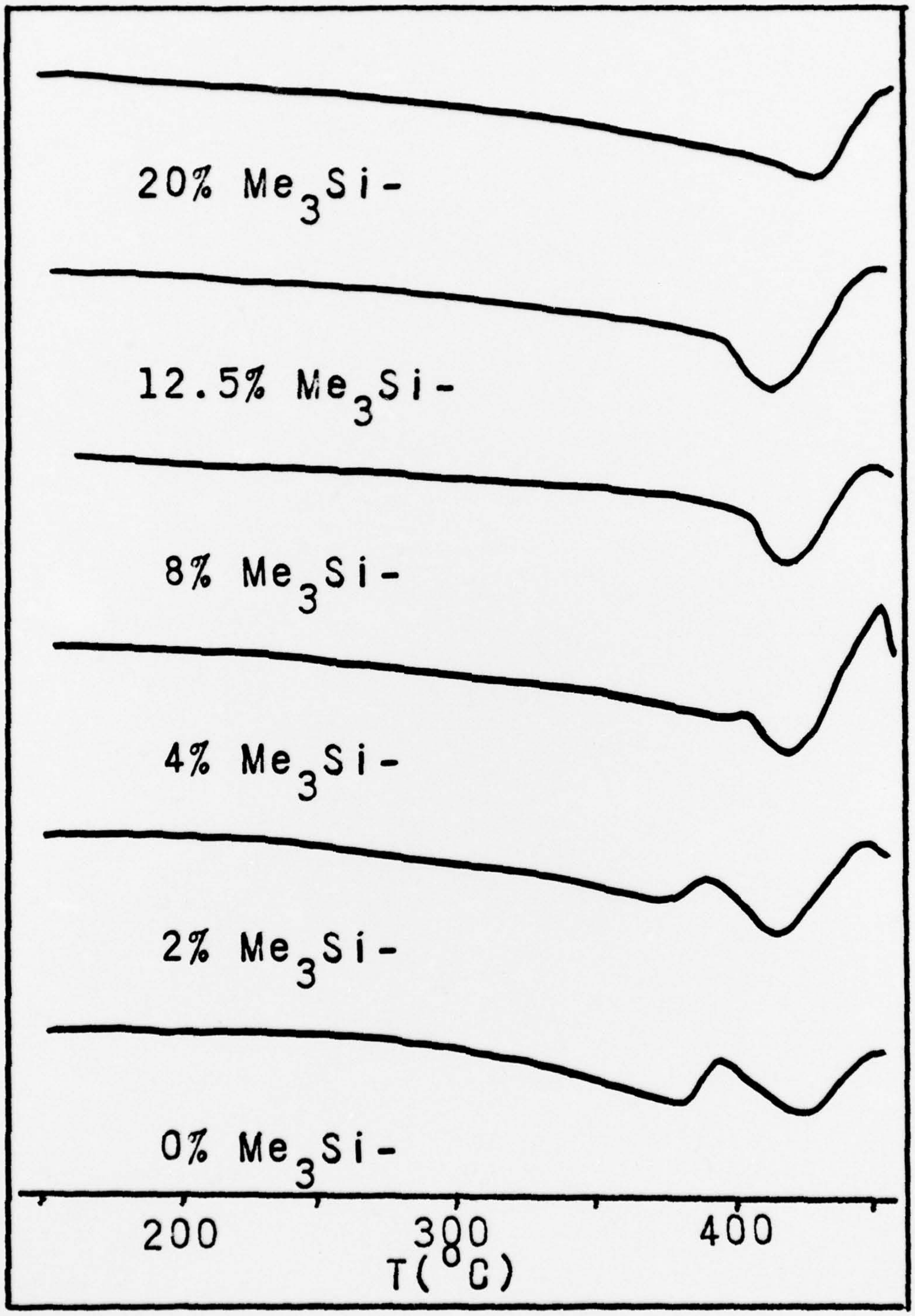

FIGURE 4: DIFFERENTIAL SCANNING CALORIMETRY OF -EtMeSi- COPOLYMERS