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AFML-TR-75-182
PART II
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ARYLENESILOXANE POLYMERS FOR USE AS HIGH-TEMPERATURE AIRCRAFT INTEGRAL FUEL TANK SEALANTS

PART II. SYNTHESIS AND PROPERTIES OF ALKYL- AND FLUOROALKYL-SUBSTITUTED ALKARYLENESILOXANE POLYMERS

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

DECEMBER 1977

TECHNICAL REPORT AFML-TR-75-182, Part II

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Harold Rosenberg

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Project Monitor

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1. REPORT NUMBER AFML-TR-75-182, Part II	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ARYLENESILOXANE POLYMERS FOR USE AS HIGH TEMPERATURE AIRCRAFT INTEGRAL FUEL TANK SEALANTS. PART II. SYNTHESIS AND PROPERTIES OF ALKYL- AND FLUOROALKYL-SUBSTITUTED ALKARYLENE-SILOXANE MONOMERS AND POLYMERS		5. TYPE OF REPORT & PERIOD COVERED Summary Report (August 1972 to August 1975) 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Eui-Won Choe and Harold Rosenberg		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 7342/734201/73420101
11. CONTROLLING OFFICE NAME AND ADDRESS AirForce Materials Laboratory (AFML/MBP) Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		12. REPORT DATE December 1977 13. NUMBER OF PAGES 118
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)

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

18. SUPPLEMENTARY NOTES

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

Alkarylsilane
Arylenesiloxane
Alkarylenesiloxane
Polymers
Organosilicon
Polysiloxanes
Polyarylenesiloxanes
Polyalkarylenesiloxanes
Fuel-tank sealants
Fluoroalkyl siloxane
Bis-silanols

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

In order to predict the molecular structures of arylenesiloxane polymers which would exhibit the optimum combinations of desired properties for high-temperature fuel-resistant sealant applications, it was found necessary to first develop pertinent structure-property correlations. To achieve the latter, new specifically-tailored monomeric alkyl- and fluoroalkyl-substituted alkarylene organosilicon compounds were synthesized and characterized. The bis-silanols were both homopolymerized as well as copolymerized with appropriate bis-aminosilanes or -disiloxanes by various condensation (continued) techniques to yield representative alkarylenesiloxane polymers. These were fully characterized with regard to chemical composition, molecular weight, thermal stability, glass-transition temperature and fuel insolubility. The polymers were also cured by means of organic peroxides and the vulcanizates evaluated for swell resistance to solvents and jet fuels.

From the characterization and evaluation data it was found possible to derive the requisite correlations for two arylenesiloxane polymer systems to permit tailoring of structure to impart needed low-temperature flexibility without sacrificing thermal and fuel resistance. Two fluoroalkyl-substituted candidate siloxane polymers, one based on a m-xylylene and one on a m-phenylene system, were selected for synthesis both as homopolymers and as copolymers containing vinyl crosslinking sites. The preparation, characterization and preliminary evaluation of the former, a polytetrasiloxanylene-m-phenylene, was successfully completed. The data obtained on this polymer strongly indicates considerable potential for achieving broader use temperature ranges with arylenesiloxane polymers than those currently available with present state-of-the-art or other candidate sealant materials.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials". It was administered under the direction of Dr. Harold Rosenberg (AFML/MBP) as Project Scientist.

This report covers research conducted from August 1972 to August 1975. This manuscript was submitted for publication by the authors in December 1977.

The authors are deeply indebted to Dr. Gerhard F. L. Ehlers, Dr. Thaddeus Helminiak and Dr. Ivan J. Goldfarb for the valuable discussions and assistance in determining the glass-transition temperatures, fuel-resistance and thermogravimetric analyses. The assistance of Ms. Mary T. Ryan and Mr. Lee D. Smithson of the Analytical Services Branch, Technical Services Division, Air Force Materials Laboratory, in determining nuclear magnetic resonance and mass spectra is greatly appreciated.

The work described in this report was conducted in the Polymer Branch laboratory by Dr. Harold Rosenberg of the Air Force Materials Laboratory and Dr. Eui-won Choe, an AFSC-NRC Postdoctoral Resident Research Associate.

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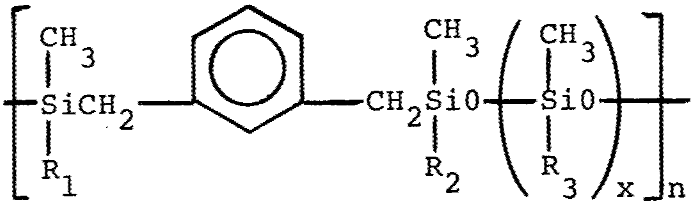
SECTION I

INTRODUCTION

The objective of this research was the synthesis and evaluation of arylene and alkarylenesiloxane polymers for high-temperature aircraft integral fuel tank sealants useful for a long service lifetime (up to 10,000 hours) over a wide temperature range (from <-40°F to 500°F). Desired chemical and physical properties for a high-temperature aircraft sealant include long-term thermal stability (>450°F), resistance to reversion at elevated temperatures in confined environments, a moderately low glass-transition temperature (<-40°F and, preferably, -65°F), excellent resistance to swell by jet fuels such as JP-4 and JP-7, excellent adhesion to aircraft metallic substrates and the capability for room-temperature cure. Oxidative stability of candidate polymers was not considered of primary significance for this application because aircraft sealants are intended for use under a nitrogen and fuel environment in the absence of oxygen. It was also desired to provide polymers with cost advantages over current high-temperature sealant-type polymers which are available commercially or under development by other organizations.

To achieve this goal, a number of new monomeric alkarylene organosilicon compounds, including bis-silanes, -silanols and -aminosilanes, were synthesized and characterized. The bis-silanols were homo- or copolymerized with appropriate aminosilanes and/or -disiloxanes by various condensation polymerization techniques into alkarylenesiloxane polymers with the following general structure:



where $R_1 = CF_3CH_2CH_2$ or CH_3

$R_3 = CF_3CH_2CH_2$ or CH_3

$x = 0, 1, 2$

These polymers were fully characterized with regard to chemical composition, molecular weight, glass-transition temperature and thermal behavior. They were then cured in order to determine their resistance to fuels and to evaluate the mechanical properties of the resulting elastomers.

SECTION II
DISCUSSION

A. Synthesis of Monomers

1. Synthesis of α,α′-Bis[hydroxymethyl-(3,3,3-trifluoropropyl)silyl]-m-xylene and Related Organosilicon Compounds

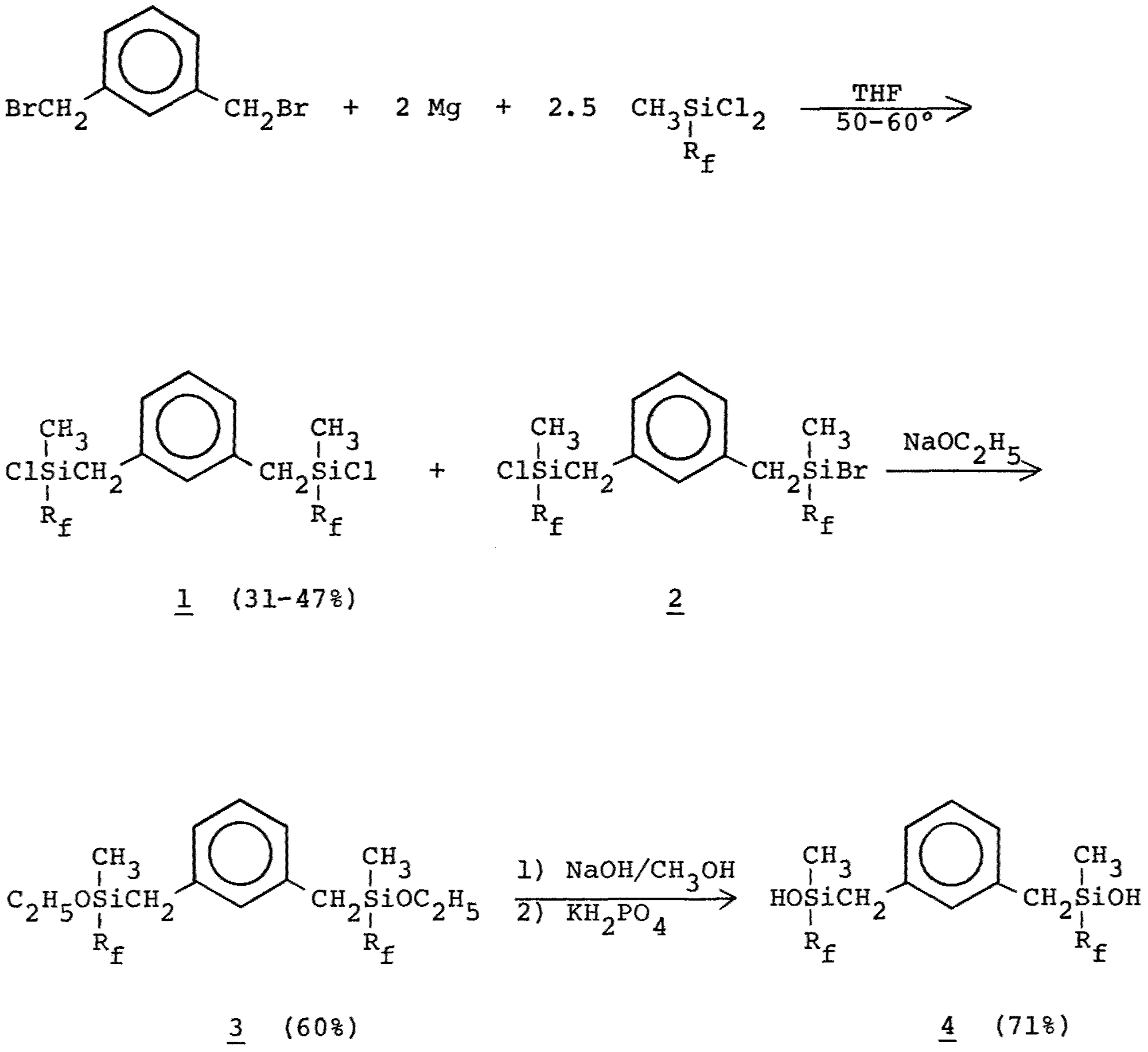
The synthetic sequence for the preparation of the key monomer, α,α′-bis[hydroxymethyl-(3,3,3-trifluoropropyl)silyl]-m-xylene (4), is shown by Scheme I. The in-situ Grignard coupling reaction of α,α′-bis(bromomethyl)-m-xylene with 2.5 moles of 3,3,3-trifluoropropylmethyldichlorosilane in tetrahydrofuran afforded α,α′-bis[chloromethyl-(3,3,3-trifluoropropyl)silyl]-m-xylene (1) in 31-47% yield, along with a small amount of α-chloromethyl(3,3,3-trifluoropropyl)silyl-α′-bromomethyl-(3,3,3-trifluoropropyl)silyl-m-xylene (2). The bis-chlorosilane 1 was converted to α,α′-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene (3) in 60% yield. The hydrolysis of the bis-ethoxy derivative 3 with sodium hydroxide in methanol afforded a 71% yield of α,α′-bis [hydroxymethyl-(3,3,3-trifluoropropyl)silyl]-m-xylene (4).

The bis-ethoxy derivative 3 was also prepared in low yield (8%, not optimized) by the in-situ Grignard coupling reaction of α,α′-bis(bromomethyl)-m-xylene and methyl(3,3,3-trifluoropropyl)chloroethoxysilane, or by the reaction of α,α′-bis[methyl (3,3,3-trifluoropropyl)silyl]-m-xylene (5) with sodium ethoxide as shown in Scheme II.

The bis-hydrosilane 5 is of considerable importance not only because it is an intermediate for the preparation of the key monomer 4, but also because it could be used as a chain extender for reaction with the vinyl-terminated oligomers or low molecular weight polymers. The bis-hydrosilane 5 was prepared as illustrated in Scheme II by two methods: a) in good yield by reduction of α,α′-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-m-xylene (1) with lithium aluminum hydride in tetrahydrofuran, and b) in poor yield by the coupling reaction of 3,3,3-trifluoropropylmagnesium bromide with α,α′-bis(methylchlorosilyl)-m-xylene (6),

Scheme I

Synthesis of α,α´-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene



1 (31-47%)

2

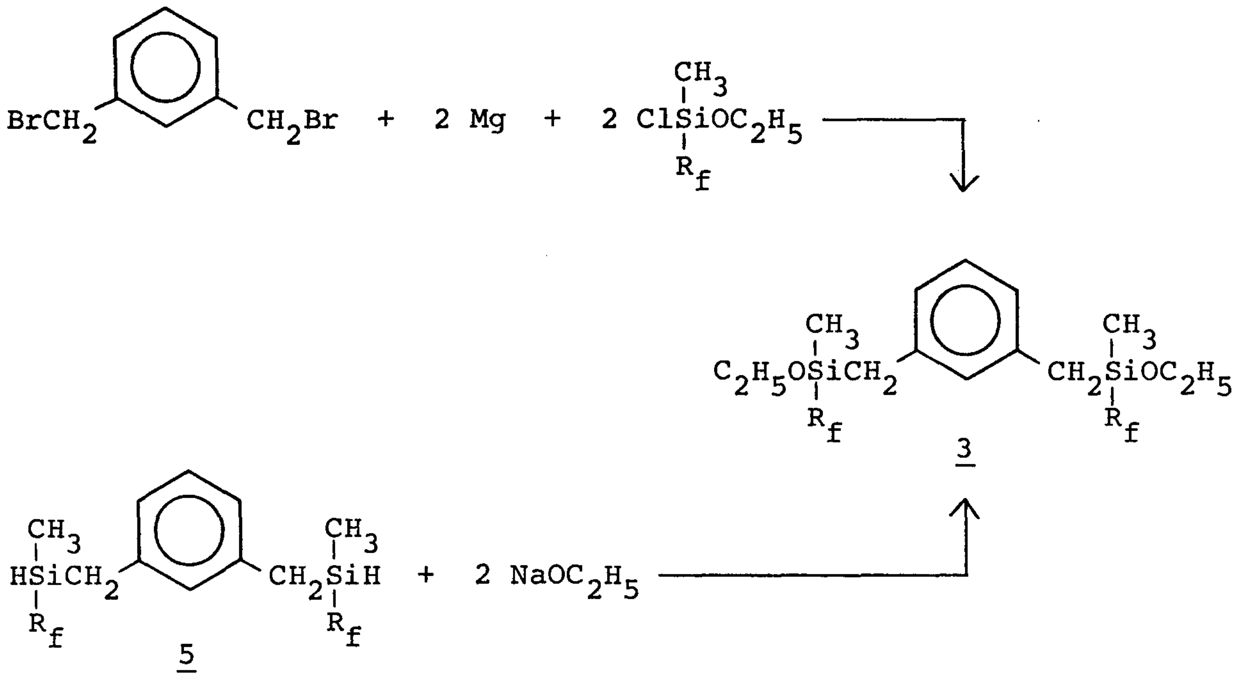
3 (60%)

4 (71%)

$R_f = CF_3CH_2CH_2$

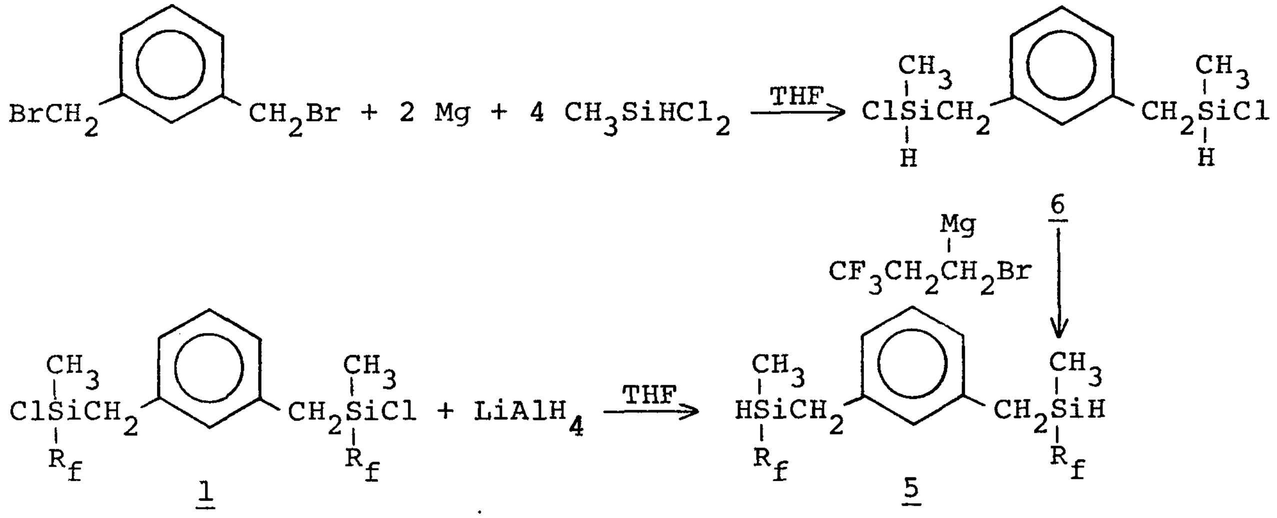
Scheme II

Alternate Synthesis of α,α´-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene



Scheme III

Synthesis of α,α´-Bis[methyl(3,3,3-trifluoropropyl)silyl]-m-xylene



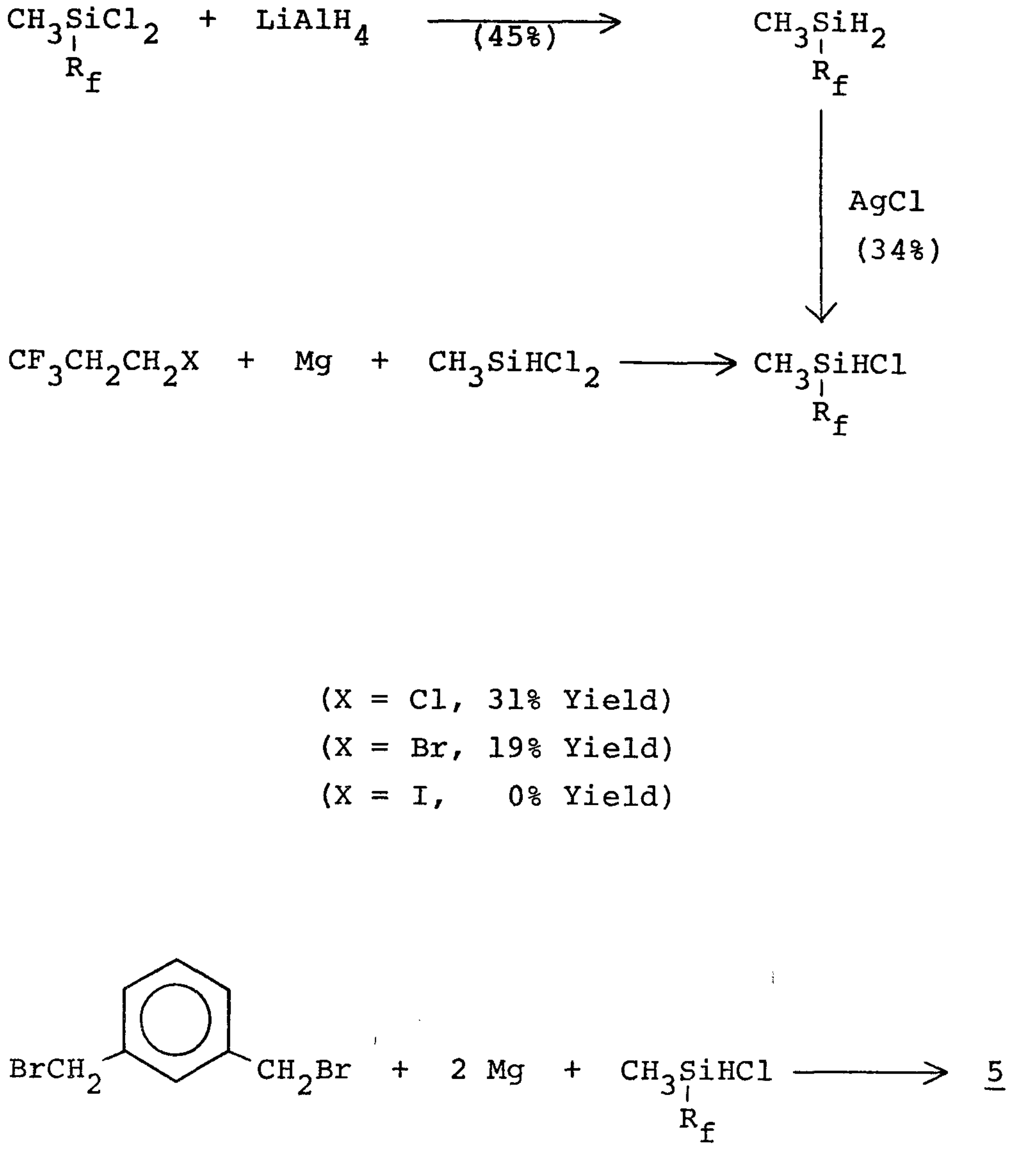
$R_f = CF_3CH_2CH_2$

obtained from the in-situ Grignard coupling reaction of α,α´-bis(bromomethyl)-m-xylene with methyldichlorosilane in tetrahydrofuran. A third alternate approach to the synthesis of the bis-silane 5 is the Grignard coupling reaction of α,α´-bis(bromomethyl)-m-xylene with methylchloro(3,3,3-trifluoropropyl)silane as shown by Scheme IV. The latter reactant, however, is not readily available. As a result, the monochlorosilane was prepared in a small quantity in this laboratory by reduction of methyl(3,3,3-trifluoropropyl)dichlorosilane with lithium aluminum hydride in n-butyl ether, followed by a partial chlorination of the resulting product, methyl(3,3,3-trifluoropropyl)silane, with a deficient amount of silver chloride. The monochlorosilane was also synthesized by reaction of 3,3,3-trifluoropropylmagnesium halides (Cl or Br) with methyldichlorosilane. The use of 3,3,3-trifluoropropylmagnesium iodide does not yield the desired product. The reaction of 3,3,3-trifluoropropylmagnesium chloride provided only the bis-silane 5, whereas 3,3,3-trifluoropropylmagnesium bromide gave a mixture of the desired product and a small amount of methyl(3,3,3-trifluoropropyl)bromosilane. The bromosilane is believed to have resulted from the halogen exchange reaction of the product with magnesium halide. However, the final coupling reaction in this third approach was not carried out due to the lack of a sufficient quantity of methyl(3,3,3-trifluoropropyl)chlorosilane.

Attempts were made to synthesize α,α´-bis[hydroxymethyl-(3,3,3-trifluoropropyl)silyl]-m-xylene (4) in one step by a direct hydrolysis of the corresponding bis-chlorosilane 1. A variety of conditions were used for the hydrolysis. The hydrolysis of the bis-chlorosilane 1 with a solution of sodium bicarbonate in water and diethyl ether at 0° afforded a mixture of cyclic dimer and trimer as evidenced by spectral analysis. Hydrolysis with potassium diacid phosphate in water and diethyl ether at 0° gave only a cyclic polysiloxane polymer, with a number average molecular weight of 6200 (DP = ~15), as evidenced by lack of absorption for SiOH in the infrared spectrum. The bis-chlorosilane 1 reacted

Scheme IV

Alternate Method for the Synthesis of α,α´-Bis[methyl(3,3,3-trifluoropropyl)silyl]-m-xylene



$$CH_3\underset{R_f}{Si}Cl_2 + LiAlH_4 \xrightarrow{(45\%)} CH_3\underset{R_f}{Si}H_2 \xrightarrow{AgCl\ (34\%)} CH_3\underset{R_f}{Si}HCl$$

$$CF_3CH_2CH_2X + Mg + CH_3SiHCl_2 \longrightarrow CH_3\underset{R_f}{Si}HCl$$

(X = Cl, 31% Yield)
(X = Br, 19% Yield)
(X = I, 0% Yield)

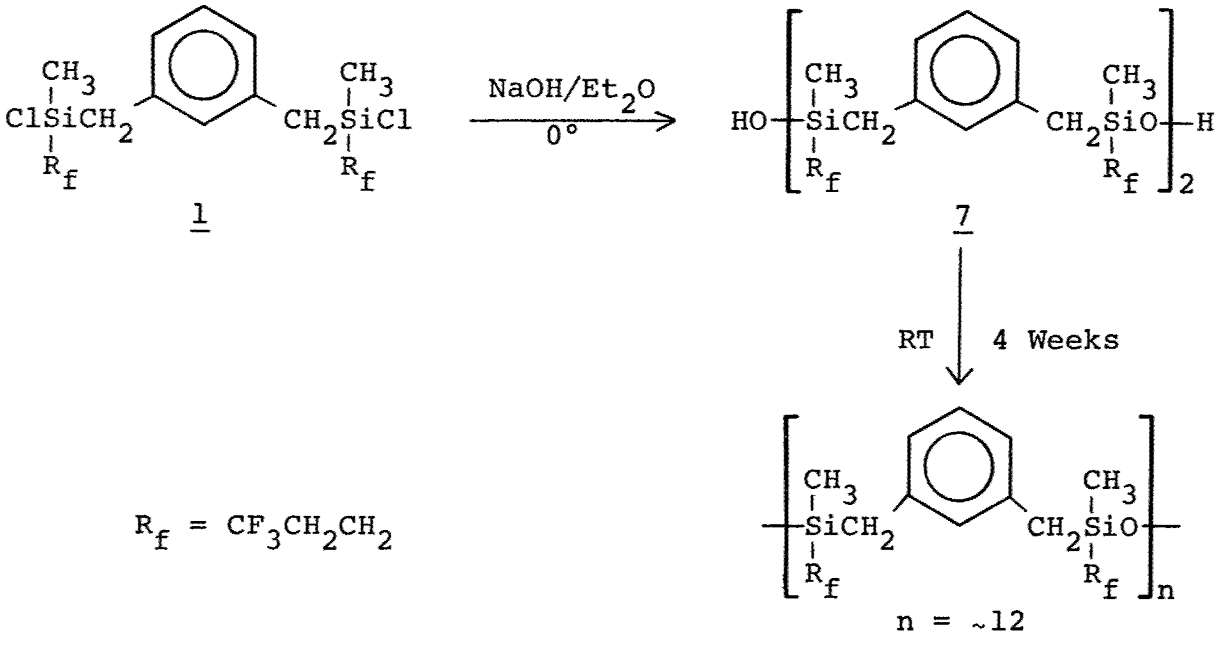
$$BrCH_2C_6H_4CH_2Br + 2\ Mg + CH_3\underset{R_f}{Si}HCl \longrightarrow \underline{5}$$

$R_f = CF_3CH_2CH_2$

with sodium hydroxide in water and diethyl ether at 0° to yield 1,3-bis[α-hydroxymethyl(3,3,3-trifluoropropyl)silyl-α´-m-xylylene]-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane, (7). The dimeric bis-silanol 7 self-condensed on standing at room temperature within four weeks into poly[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxanylene-m-xylylene] with a DP (degree of polymerization) of ∼12 as indicated in Scheme V.

Scheme V

Synthesis of 1,3-Bis[α-hydroxymethyl(3,3,3-trifluoropropyl)silyl-α´-m-xylylene]-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-disiloxane

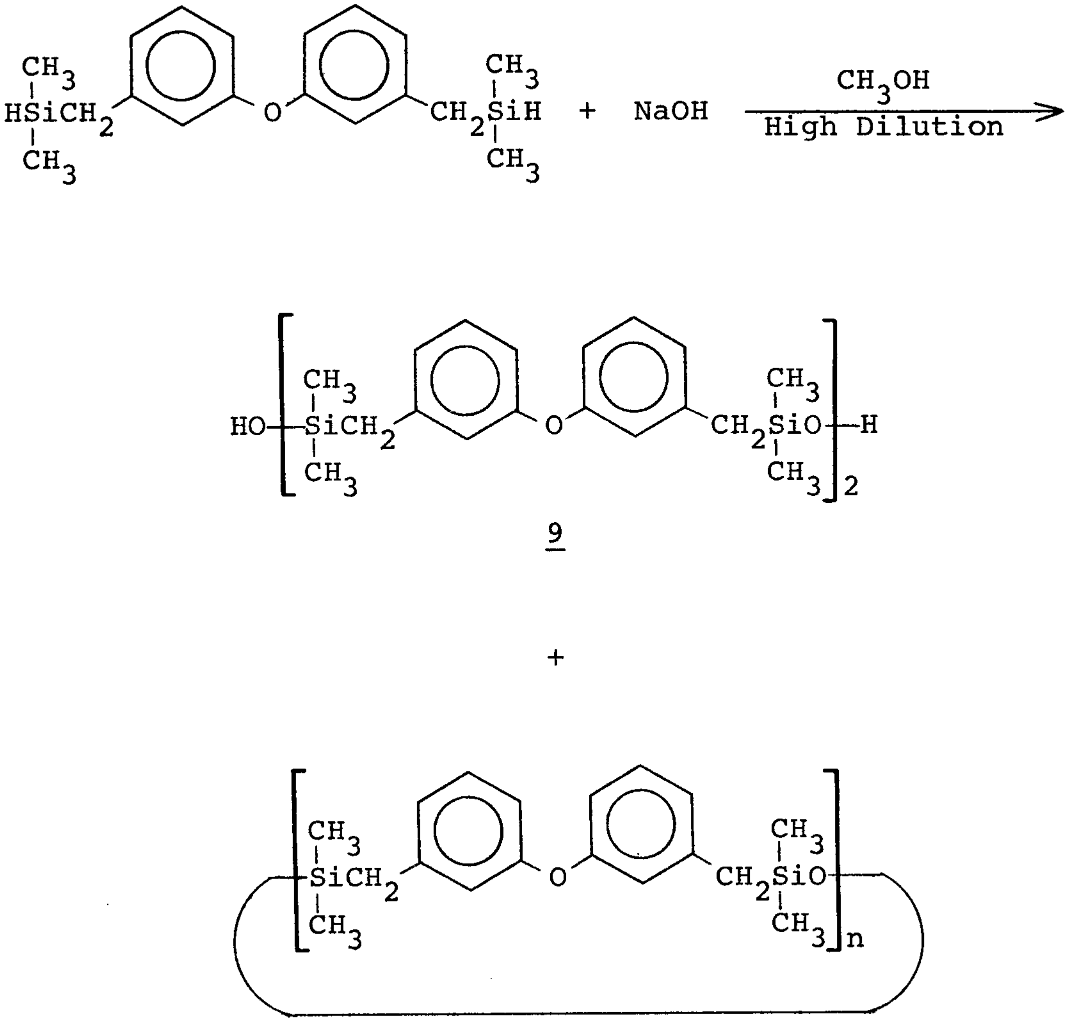


2. Synthesis of 1,3-Bis[(dimethylhydroxysilyl)methylene-3,3´-oxydiphenylenemethylene]-1,1,3,3-tetramethyldisiloxane

The use of a high dilution technique for the reaction of α,α´-bis(dimethylhydrogensilyl)-m-tolyl ether (8) with a solution

2. Synthesis of 1,3-Bis[(dimethylhydroxysilyl)methylene-3,3´-oxydiphenylenemethylene]-1,1,3,3-tetramethyldisiloxane

The use of a high dilution technique for the reaction of α,α´-bis(dimethylhydrogensilyl)-m-tolyl ether (8) with a solution of sodium hydroxide in methanol provided a 67% yield of 1,3-bis[(dimethylsilylhydroxysilyl)methylene-3,3´-oxydiphenylenemethylene]-1,1,3,3-tetramethyldisiloxane (9), a 6.5% yield (GLC analysis) of 2,4-disila-3,12-dioxa-2,2,4,4-tetramethyl [5.1]metacyclophane (10), and traces of cyclic compounds 11 and 12.



9

10, n=1

11, n=2

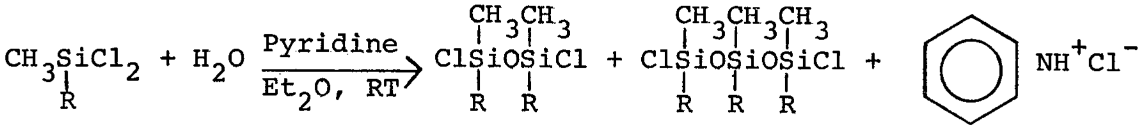
12, n=3

3. Synthesis of Bis(dimethylamino)methyl-3,3,3-trifluoropropylsilane, 1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane, and Other Related Compounds

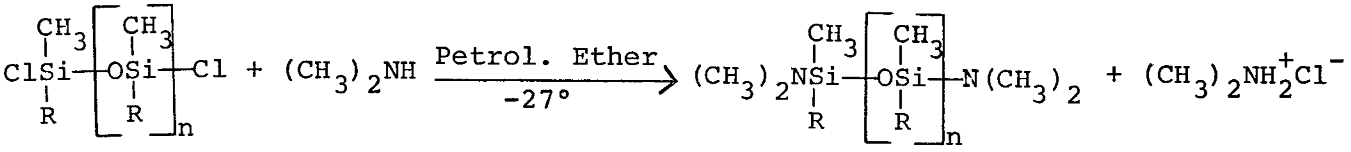
Comonomers needed for copolymerization with the bis-silanols 4, 7 and 9 to enable the preparation of alkarylene-siloxanylene polymers of interest were bis(dimethylamino)methyl-3,3,3-trifluoropropylsilane (15a) and 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane (16a).

The bis-aminosilane 15a was prepared in 64% yield by the reaction of methyl-3,3,3-trifluoropropyldichlorosilane with anhydrous dimethylamine at -27° in petroleum ether. The bis(amino)-disiloxane 16a was similarly prepared in 67.7% yield from anhydrous dimethylamine and 1,3-dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane (13). The latter compound, 13, was obtained by a controlled hydrolysis of methyl(3,3,3-trifluoropropyl)dichlorosilane which yielded a mixture together with 1,5-dichloro-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxane (14) separable by fractional distillation.

Similar reactions of dimethylamine with dimethyldichlorosilane, and with 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, provided bis(dimethylamino)dimethylsilane (15b) (in 52.7% yield) and 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane (16b) (in 61.2% yield).



13, R = $CF_3CH_2CH_2$ 14, R = $CF_3CH_2CH_2$



$$\mathrm{ClSi(CH_3)(R)}\!-\![\mathrm{OSi(CH_3)(R)}]_n\!-\!\mathrm{Cl} + (\mathrm{CH_3})_2\mathrm{NH} \xrightarrow[-27^\circ]{\text{Petrol. Ether}} (\mathrm{CH_3})_2\mathrm{NSi(CH_3)(R)}\!-\![\mathrm{OSi(CH_3)(R)}]_n\!-\!\mathrm{N(CH_3)_2} + (\mathrm{CH_3})_2\mathrm{NH_2^+Cl^-}$$

	R = $CF_3CH_2CH_2$	R = CH_3
n = 0	15a	15b
n = 1	16a	16b

B. Synthesis and Characterization of Alkarylenesiloxanylene Polymers

1. Poly(disiloxanylene-*m*-xylylenes)

In an effort to prepare low molecular weight model disiloxanylene polymers and to evaluate their thermal properties, both dimethyl- and methyl(3,3,3-trifluoropropyl-substituted *m*-xylylene systems were investigated. α,α′-Bis(dimethylhydroxysilyl)-*m*-xylene (17) was selected and studied initially as a monomer for a homocondensation polymerization with one weight-percent (based on the bis-silanol) of a suitable catalyst. Two catalysts, n-hexylamine 2-ethylhexoate (HA-EHA) and 1,1,3,3-tetramethylguanidine (TMG), were investigated and their use reported previously in our earlier report (AFML-TR-75-182, Part I, December 1976) for the condensation polymerization of the bis-silanol 17. Two additional catalysts, 1,1,3,3-tetramethylguanidine trifluoroacetate (TMG-TFA) and 1,1,3,3-tetramethylguanidine 2-ethylhexoate (TMG-EHA), were investigated for the homopolymerization of the bis-silanol 17 during the investigation covered by this report.

The polymerization was carried out by refluxing the mixture of the bis-silanol 17 and a suitable catalyst in benzene for five hours, removing the solvent and water formed during this period azeotropically, and by then heating the mixture for many hours at 160° under reduced pressure. The intrinsic viscosities and number average molecular weights (as determined by either high speed membrane osmometry or vapor phase osmometry) of the resulting homopolymers from both the current as well as earlier investigation are listed in Table 1. The homopolymerization of the bis-silanol 17 in the presence of TMG-EHA catalyst was carried out successfully to yield the polymer with the highest molecular weight whereas in the presence of TMG alone, the polymer with the lowest molecular weight was obtained.

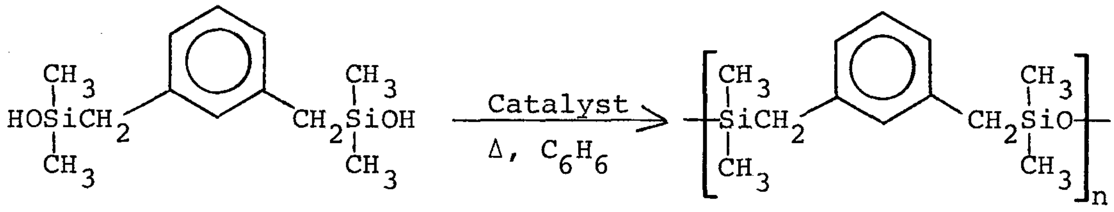
Table I

Viscosities and Molecular Weights of Poly[1,1,3,3-tetramethyldisiloxanylene-*m*-xylylene] Prepared from α,α'-Bis(dimethylhydroxysilyl)-*m*-xylene and a Catalyst

Catalyst	[η], dl/g, 30°, Toluene	Molecular Weight	
TMG	-	2560-3456	(VPO)
TMG-TFA	0.35	>25,000	
HA-EHA	0.43	38,878	(MO)
TMG-EHA	0.51	41,750	(MO)

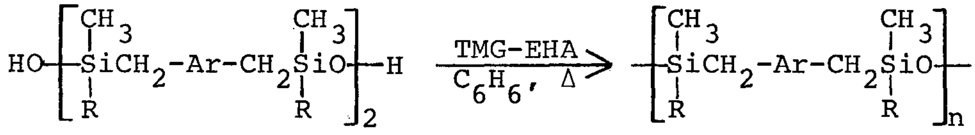
TMG = 1,1,3,3-Tetramethylguanidine
EHA = 2-Ethylhexanoic Acid
HA = *n*-Hexylamine

VPO = Vapor Phase Osmometry
MO = Membrane Osmometry



17

18a



$$\mathrm{HO}\left[\overset{CH_3}{\underset{R}{\mathrm{Si}}}CH_2\text{-Ar-}CH_2\overset{CH_3}{\underset{R}{\mathrm{Si}}}\mathrm{O}\right]_2\mathrm{H} \xrightarrow[C_6H_6,\ \Delta]{\text{TMG-EHA}} \left[\overset{CH_3}{\underset{R}{\mathrm{Si}}}CH_2\text{-Ar-}CH_2\overset{CH_3}{\underset{R}{\mathrm{Si}}}\mathrm{O}\right]_n$$

7, Ar = 1,3-C_6H_4- and R = $CF_3CH_2CH_2$ 18b, Ar = 1,3-C_6H_4- and R = $CF_3CH_2CH_2$

9, Ar = 3,3´-C_6H_4-O-C_6H_4- and R = CH_3 18c, Ar = 3,3´-C_6H_4-O-C_6H_4-

Poly[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-disiloxanylene-m-xylylene] (18b) was prepared by four different methods: a) by homopolymerization of the bis-silanol 7 with 1,1,3,3-tetramethylguanidine 2-ethylhexanoate (TMG-EHA) as catalyst, b) by thermal polymerization of the bis-silanol 7 at 500° and under high vacuum, c) by copolymerization of α,α´-bis[chloromethyl-(3,3,3-trifluoropropyl)silyl]-m-xylene (1) and α,α´-bis[methoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene with 1.5% anhydrous ferric chloride at 200°, and d) by reaction of the bis-chlorosilane 1 with one equivalent of absolute ethanol, followed by polymerization of the resulting mixture in the presence of 1.5% ferric chloride. The viscosities and molecular weights of the resulting polymer 18b are summarized in Table II.

Table II

Viscosities and Molecular Weights of Poly[1,3-dimethyl-1,3-bis-(3,3,3-trifluoropropyl)disiloxanylene-m-xylylene] (18b) and Poly(1,1,3,3-tetramethyldisiloxanylenemethylene-3,3′-oxydiphenylenemethylene) (18c)

Polymer	Starting Reactants(s)	Catalyst	[η], dl/g, 30°, Toluene	Molecular Weight	
18b	7	TMG-EHA	0.142	45,600	(MO)
18b	7	Thermal	Not determined due to poor solubility		
18b	1 + BMX	$FeCl_3$	0.192	-	
18b	1 + C_2H_5OH	$FeCl_3$	-	7400	(VPO)
18c	9	TMG-EHA	0.131	7200	(VPO)

TMG = 1,1,3,3-tetramethylguanidine

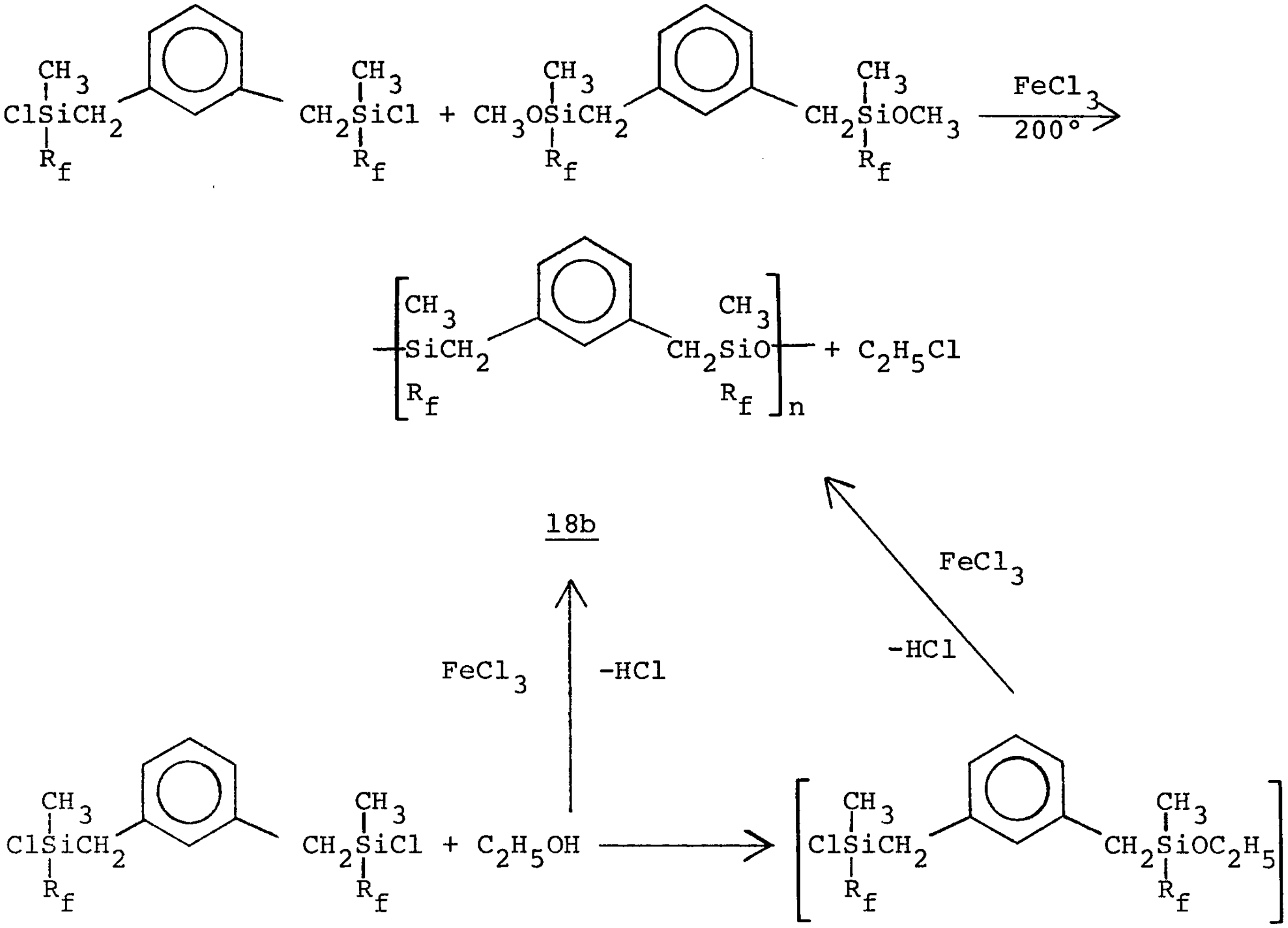
EHA = 2-ethylhexanoic acid

BMX = α,α′-bis[methoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

VPO = vapor phase osmometry

MO = membrane osmometry

1,3-Bis[(dimethylhydroxysilyl)methylene-3-oxydiphenylenemethylene]-1,1,3,3-tetramethyldisiloxane (9) was readily polymerized, with 1,1,3,3-tetramethylguanidine 2-ethylhexanoate as catalyst, to poly(1,1,3,3-tetramethyldisiloxanylenemethylene-3-oxydiphenylenemethylene), (18c).



2. Poly[trisiloxanylene-*m*-xylylenes] and Poly[tetrasiloxanylene-*m*-xylylenes]

A variety of new alkarylenetrisiloxanylene and alkarylenetetrasiloxanylene polymers containing methyl and polyfluoroalkyl groups were prepared by utilizing the bis-silanol—diaminosilane reaction.[12] This reaction is an excellent and versatile method for the synthesis of both dimethyl- amd methyl(3,3,3-trifluoropropyl)-substituted alkarylene siloxanylene polymers having the alkarylene units alternating regularly with alkyl and fluoroalkyl- containing trisiloxanylene or tetrasiloxanylene linkages in a polymer chain.

The reaction of α,α′-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene (4) with one equivalent of bis(dimethylamino)methyl(3,3,3-trifluoropropyl)silane (15a) in toluene at reflux temperature provided poly[1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene] (19d) in quantitative yield after evolution of dimethylamine at temperatures above 70°. Poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene (19c) was obtained similarly from the reaction of bis-silanol 4 and bis(dimethylamino)dimethylsilane.

Poly[1,1,3,3,5,5-hexamethyltrisiloxanylene-m-xylylene] (19a) and poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)-trisiloxanylene-m-xylylene] (19b) were also prepared in the same manner by reaction of α,α′-bis(dimethylhydroxysilyl)-m-xylene (17) with bis(dimethylamino)dimethylsilane or bis(dimethylamino)-methyl(3,3,3-trifluoropropyl)silane, respectively.

The molecular weights of these alkarylenetrisiloxanylene polymers were optimized, but could be controlled easily by variation of the ratio of the bis-silanol to the bis-aminosilane. The intrinsic viscosities of these polymers are listed in Table III.

In order to introduce some functionality into alkarylene-siloxanylene polymer chain for crosslinking or chain extension of low molecular weight polymers, the vinyl group was selected as the most appropriate functionality for this study. While there are many methods for introduction of vinylsilyl groups onto siloxane polymers, the most convenient method for introduction of a small amount of vinyl groups into the fluorinated alkarylene-trisiloxanylene polymers was found to involve the use of a mixture of the appropriate bis-aminosilane and a small quantity of vinylsubstituted bis-aminosilane, such as vinylmethylbis(dimethylamino)-silane. Thus, the reaction of the bis-silanol 4 with a mixture of methyl(3,3,3-trifluoropropyl)bisdimethylaminosilane and 3% of vinylmethylbisdimethylaminosilane provided poly[1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene] containing 3% vinylmethylsilyl groups (19e).

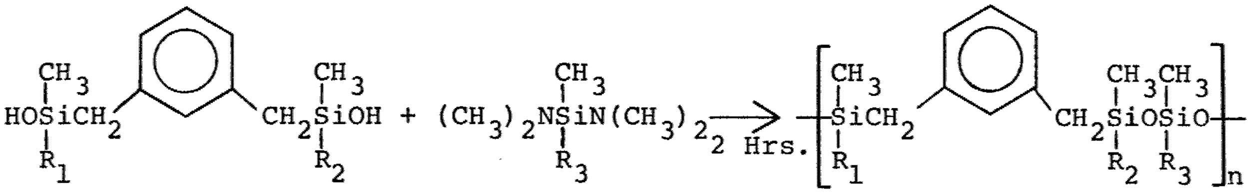
Poly[1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3,3,3-trifluoropropyl)tetrasiloxanylene-m-xylylene] (20c) was similarly prepared in toluene at 110° from the bis-silanol 4 and 1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-1,3-bis(dimethylamino)disiloxane (16a). Copolymerization of the bis-silanol 17 with 1,1,3,3-tetramethyl-1,3-bis(dimethylamino disiloxane (16b) or with the diaminodisiloxane 16a gave, in quantitative yield, poly[1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-m-xylylene] (20a) or poly[1,1,3,5,7,7-hexamethyl-3,5-bis(3,3,3-trifluoropropyl)tetrasiloxanylene-m-xylylene] (20b), respectively.

The viscosities and number average molecular weights of these polymers are listed in Table IV.

C. Thermal Properties of Alkarylenesiloxanylene Polymers

It has been well known that commercial polydimethylsiloxane decomposes and reverts into low molecular weight cyclic hexamethyltrisiloxane and cyclic octamethyltetrasiloxane on heating at 300° or below. Furthermore, it has previously been reported that the thermal stability of soloxane polymers could be improved by incorporation of arylene segments between two silicon atoms in a polysiloxane chain, and/or by reduction of the number of siloxy groups between two aromatic rings in the arylene-siloxane polymers.[9,13,14,15]

In this report our results on the effects of introduction of m-xylylene segments, of varying the chain length of siloxanylene moities, and of the introduction of polyfluoroalkyl substitutes on the silicon atoms, on the thermal and physical properties of both the alkyl and fluoroalkyl-substituted alkarylenesiloxanylene polymers are described.



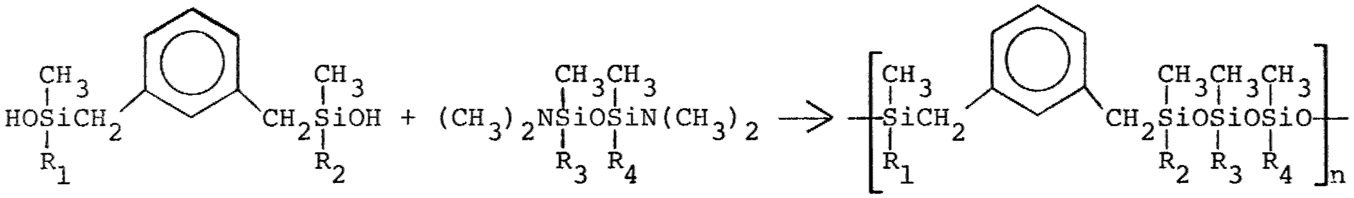
19a $R_1 = R_2 = R_3 = R_4 = CH_3$

19b $R_1 = R_2 = CH_3$, $R_3 = R_f$

19c $R_1 = R_2 = R_f$, $R_3 = CH_3$

19d $R_1 = R_2 = R_3 = R_f$

19e $R_1 = R_2 = R_f$,
$R_3 = 97\%R_f + 3\%CH_2 = CH$



20a $R_1 = R_2 = R_3 = R_4 = CH_3$

20b $R_1 = R_2 = CH_3$,
$R_3 = R_4 = R_f$

20c $R_1 = R_2 = R_3 = R_4 = R_f$

$R_f = CF_3CH_2CH_2$

Table III

Physical and Thermal Properties of Poly[trisiloxanylene-m-xylylenes]

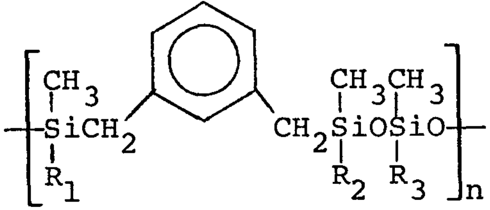
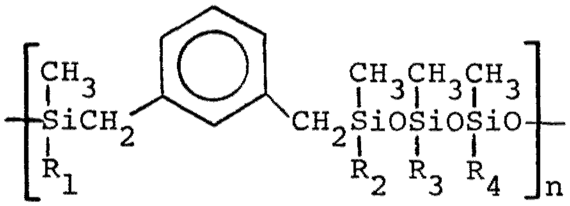
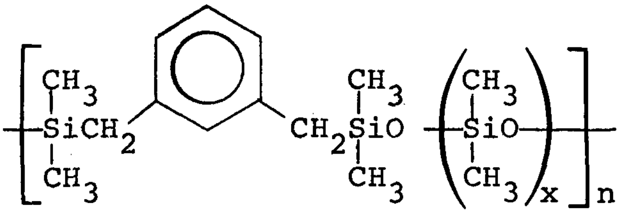
Polymer 	[η], dl/g, 30°, Toluene	Molecular Weight, $\overline{M}_n$	T_g, °C	TGA °C. at % Weight Loss		
				10%	25%	50%
19a = $R_1 = R_2 = R_3 = CH_3$	0.355	14,500 (C_6H_6)	-62	536.7	557.2	573
19b = $R_1 = R_2 = CH_3$, $R_3 = R_f$	0.243	33,000 (C_6H_6)	-52	494.4	521	538
19c = $R_1 = R_2 = R_f$, $R_3 = CH_3$	0.11	21,000 (C_6H_6)	-44	453	472	493
19d = $R_1 = R_2 = R_3 = R_f$	0.08 (at 45°)		-35	449.7	471	491.4
19e = $R_1 = R_2 = R_f$, $R_3 = 97\% R_f +$ $3\% CH_2 = CH$		21,000 (THF)	-33.5	440.7	471.1	493

Table IV

Physical and Thermal Properties of Poly[tetrasiloxanylene-*m*-xylylenes]

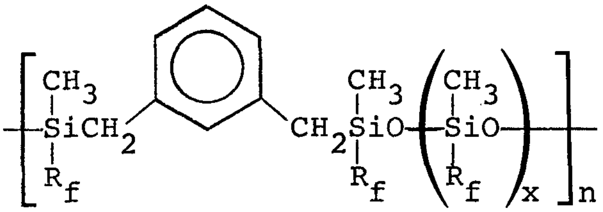
	Polymer 	$\eta_{inh.}$, dl/g, 30°, THF	Molecular Weight, $\overline{M}_n$ (VPO)	T_g, °C	TGA °C. at % Weight Loss 10%	 25%	 50%
20a	$R_1 = R_2 = R_3 = R_4 = CH_3$		14,000 (C_6H_6)	-77	508	538	563
20b	$R_1 = R_2 = CH_3$, $R_3 = R_4 = R_f$	0.08	13,000 (THF)	-59	478	504	529
20c	$R_1 = R_2 = R_3 = R_4 = R_f$	0.142	22,000	-38	446	473	499

Using thermogravimetric analysis, programmed tnermograms, obtained at a heating rate of 5° per minute, for polydimethylsiloxane and all-methylated poly[siloxanylene-m-xylylene] polymers with the general structure of



in which the chain length of the dimethylsiloxanyl linkage was varied from disiloxanylene (x = 0) to tetrasiloxanylene (x = 2) are shown in Figure 1. In this series, the alkarylenesiloxanylene polymer 19a with a hexamethyl trisiloxanylene linkage showed higher thermal stability than those of polymers with tetramethyldisiloxanylene, 18a, and octamethyltetrasiloxane, 20a moities. This is consistent with the result reported for the silphenylene-siloxane polymer series. However, the latter two polymers with disiloxanylene or trisiloxane linkages, 18a and 20a, did not show significant differences in thermal stability from 19a or from each other. It is apparent that the thermal stabilities of poly[siloxanylene-m-xylylene] polymers, 18a, 19a, and 20a, are considerably higher than that of the polydimethylsiloxane, with molecular weight of 172,528, which was prepared by the ring-opening reaction of hexamethylcyclotrisiloxane with tetramethylammonium hydroxide.

The effect of varying the chain length of methyl(3,3,3-trifluoropropyl)siloxanylene segments on the thermal stability of fluoroalkyl-containing poly[polysiloxanylene-m-xylylenes] with the general structure of



$R_f = CF_3CH_2CH_2$

Figure 1. Thermogravimetric analyses of polydimethylsiloxane (curve O), and poly[siloxanylene-m-xylylenes] with the general structure

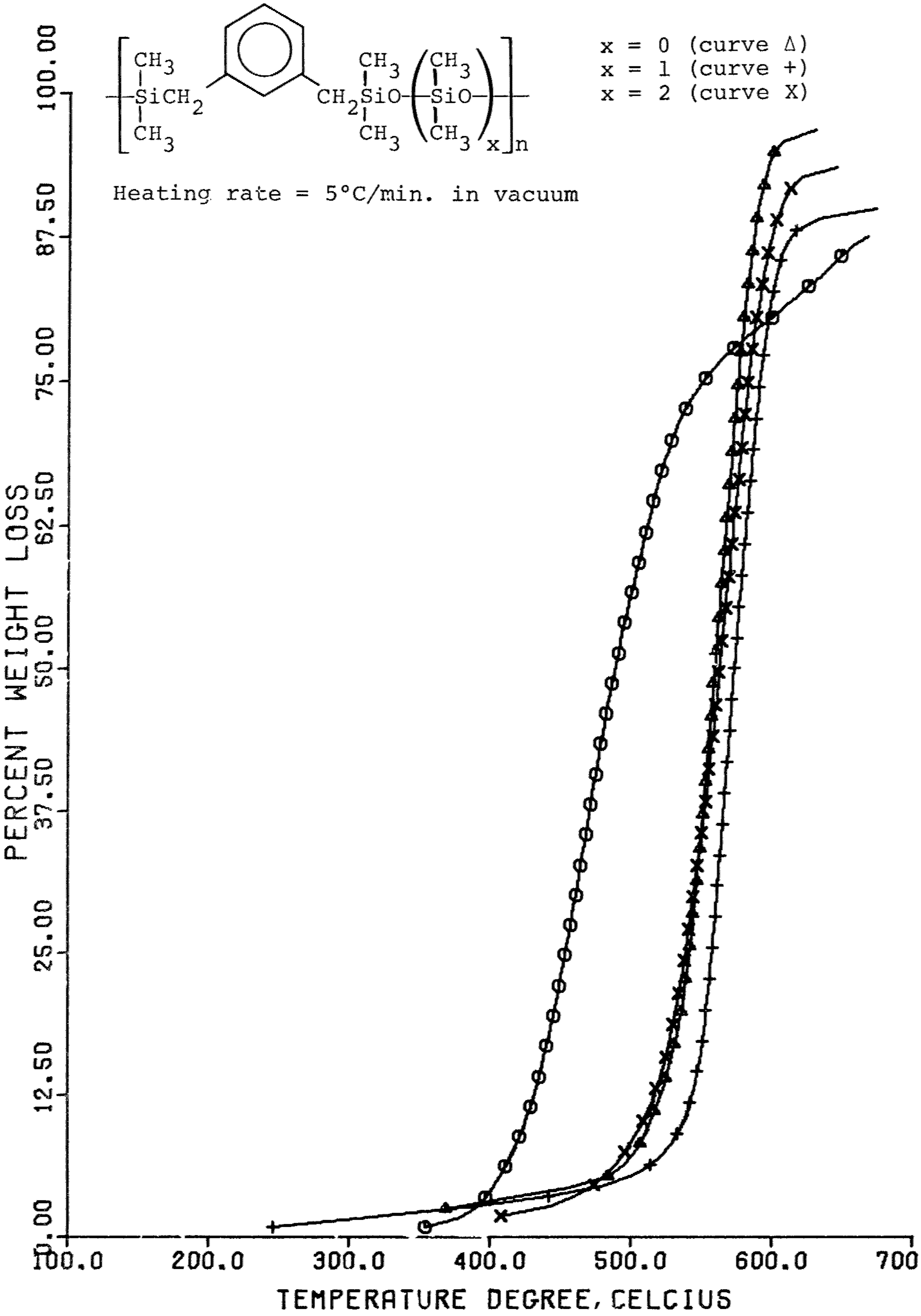
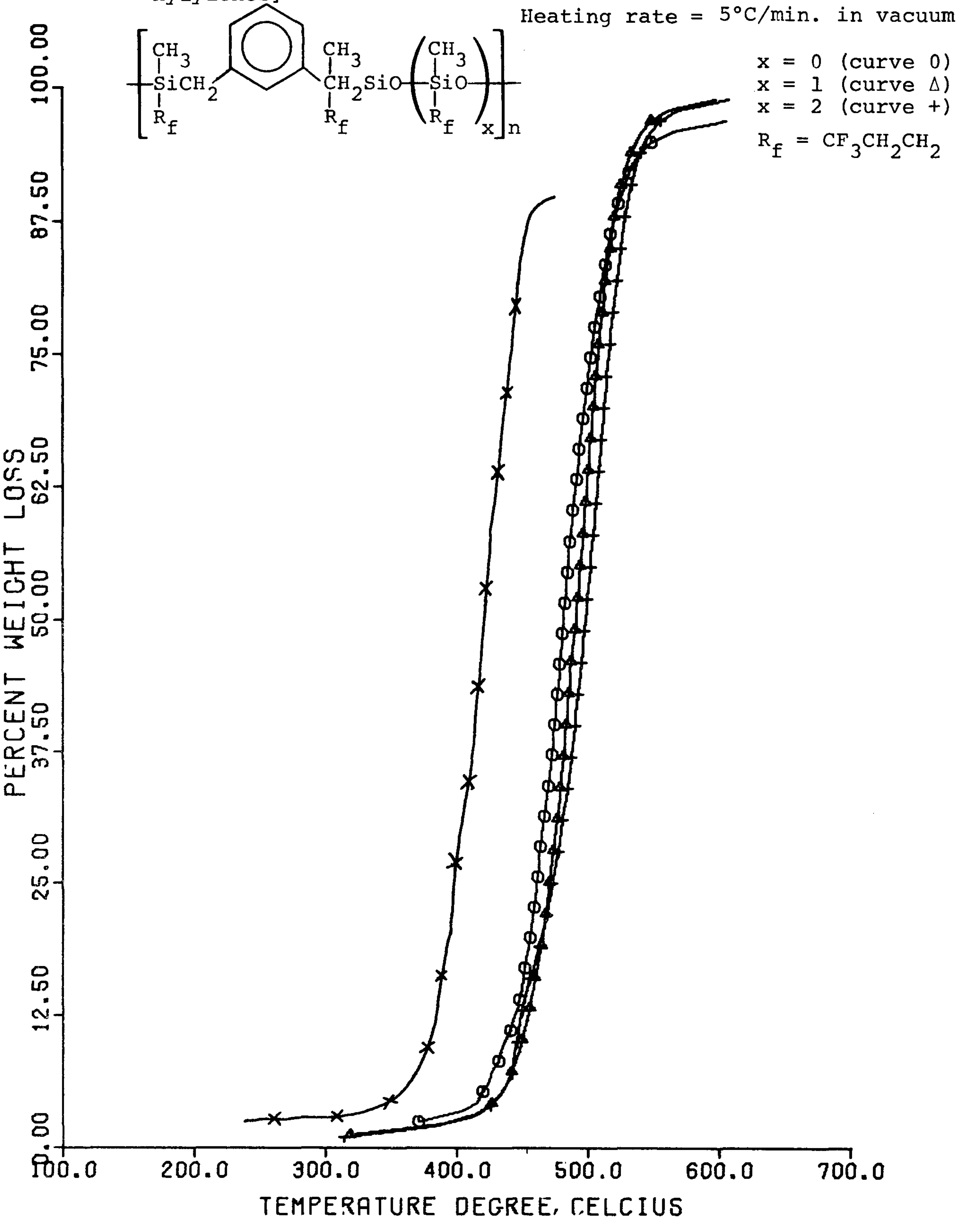


Figure 2. Thermogravimetric analyses of poly[methyl(3,3,3-trifluoropropyl)siloxane] (curve X), and poly[siloxanylene-*m*-xylylenes]



is shown in Figure 2. The increase in the chain length of methyl(3,3,3-trifluoropropyl)siloxanylene linkages from disiloxanylene (x = 0) to tetrasiloxanylene (x = 2) resulted in insignificant change in the thermal stability. However, it is apparent that the thermal stability of fluorinated, i.e. fluoroalkyl-substituted, poly[siloxanylene-m-xylylenes], 18b, 19d and 20c, are considerably higher than that of poly[methyl-(3,3,3-trifluoropropyl)siloxane].

The thermograms for poly[trisiloxanylene-m-xylylenes] (19a, 19b, 19c, 19d); poly[tetrasiloxanylene-m-xylylenes] (20a, 20b, 20c), with variation of numbers and positions of the 3,3,3-trifluoropropyl groups on the silicon atoms, are shown, together with that for Dow-Corning's FCS-210, in Figures 3 and 4. It is obvious that the substitution of 3,3,3-trifluoropropyl groups for methyl groups decreases the thermal stability of the polymers. In the trisiloxanylene-m-xylylene polymer series, the replacement of one methyl with one 3,3,3-trifluoropropyl group at the 3-position or on the middle silicon atom lowers the heat stability by approximately 40 degrees from that of the all-methylated analog, 19a. The substitution of two 3,3,3-trifluoropropyl groups for two methyl groups attached to the silicon atoms bearing a benzylic group lowers the thermal stability of the polymer by approximately 80-86 degrees from that of the all-methylated analog, 19a. The heat stability remains at this level upon further replacement of a methyl group with an additional 3,3,3-trifluoropropyl group, as observed for the polymer 19d. Incorporation of a fourth 3,3,3-trifluoropropyl group in place of another methyl group in poly[tetrasiloxanylene-m-xylylene], 20c, resulted in the same thermal stability as those of the trisiloxane-m-xylylene polymers with either two or three 3,3,3-trifluoropropyl groups, 19c and 19d. In the tetrasiloxanylene-m-xylylene polymer series, the replacement of two methyl groups with two 3,3,3-trifluoropropyl groups on the silicon atoms which do not bear a benzylic unit resulted in better thermal stability than

Figure 3. Thermogravimetric analyses of FCS-210 (curve ◈) and poly[trisiloxanylene-m-xylylenes], with the general general structure

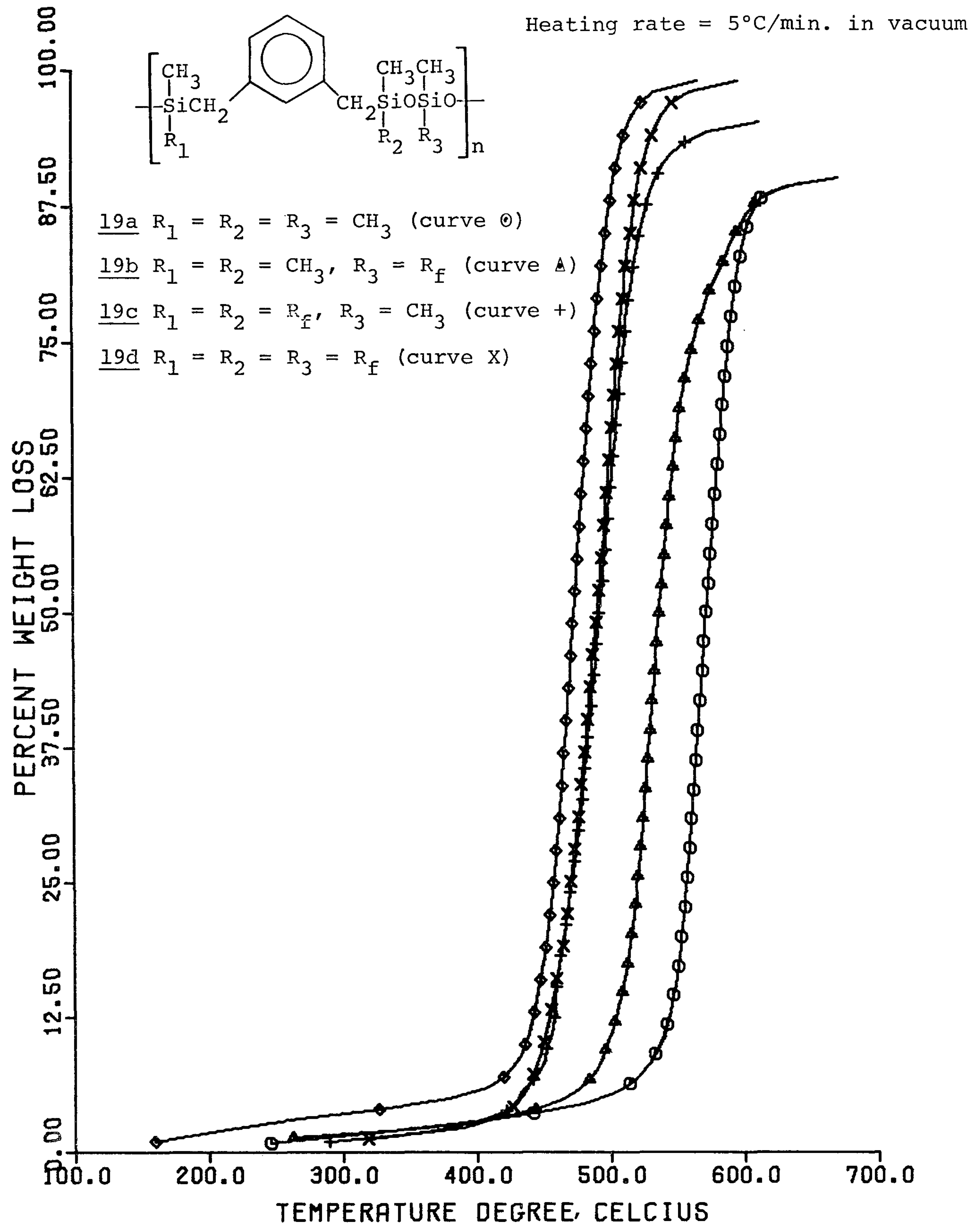
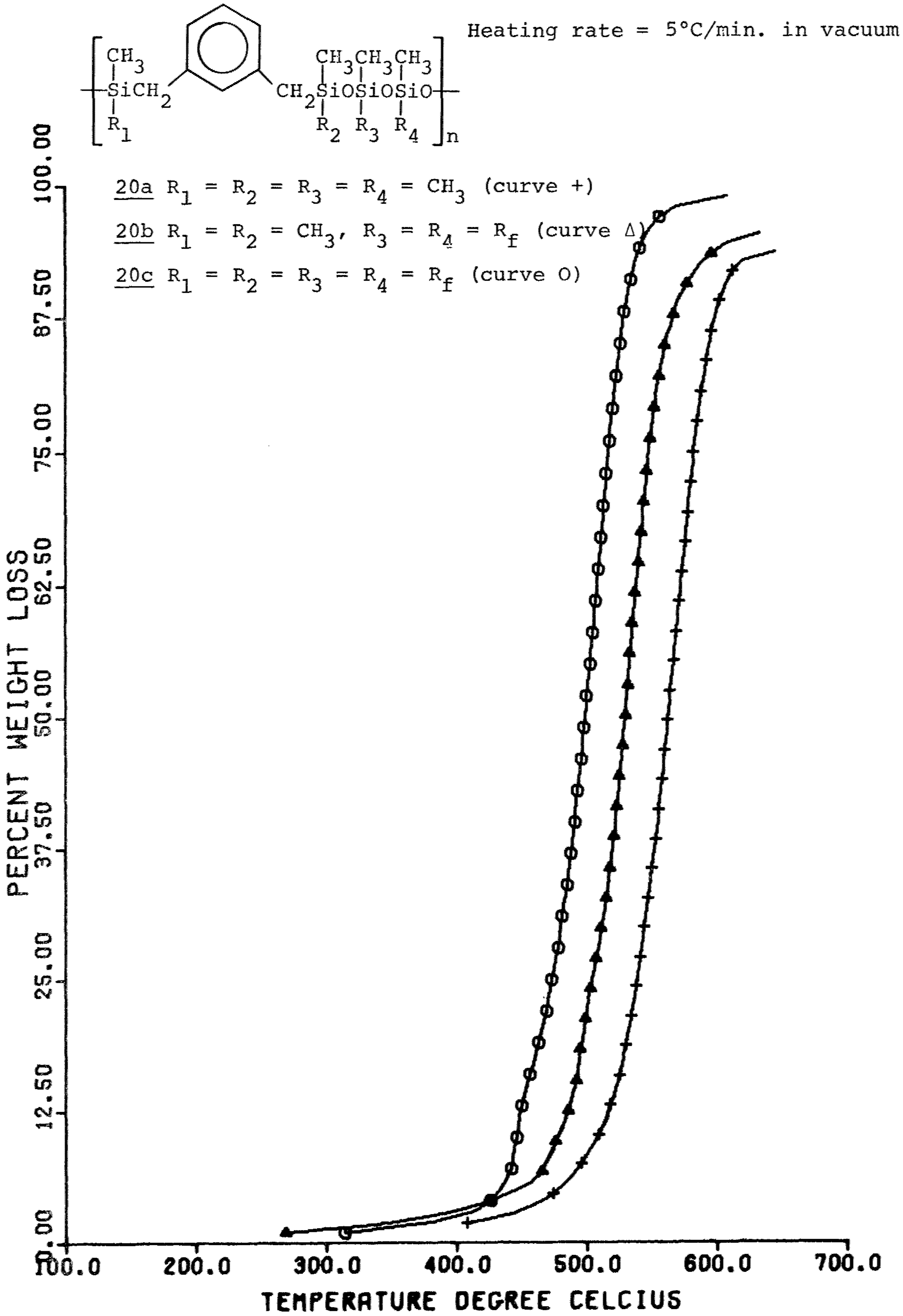


Figure 4. Thermogravimetric analyses of poly[tetrasiloxanylene-*m*-xylylenes]



that of poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)-trisiloxanylene-m-xylylene] (19c), in which the two fluorinated groups are attached to the silicon atoms bearing a benzylic unit. In this tetrasiloxanylene series, the thermal stability of polymers relative to that of the all-methylated analog, 20a, decreased by 62-65 degrees due to the substitution of four 3,3,3-trifluoropropyl, and by 30-34 degrees due to two 3,3,3-trifluoropropyl groups which are not adjacent to the benzylic unit.

It is apparent that the thermal stability of the fluoroalkyl-substituted polymers is greatly dependent on the position to which the fluorinated groups are attached, and that it appears to be almost independent of the number of fluoroalkyl groups. The incorporation of the fluorinated groups on silicon atoms which do not bear a benzylic or aromatic ring provides some improvement in the thermal stability over that of polymers where the fluorinated groups are attached to silicon atoms bearing a benzylic or aromatic ring.

The importance of the vinyl functionality of some polymers was mentioned earlier in connection with incorporation of possible sites for cross-linking and chain extension. The effect of the presence of a small amount of these vinyl groups on the thermal stability was investigated. The thermogravimetric analyses of poly[1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene] with and without 3% vinyl functionality into the polymer backbone does not affect the thermal stability. The same result was observed for poly[methyl-(3,3,3-trifluoropropyl)siloxane] with and without 3% vinyl groups. Figures 5 and 6 show the effect of vinyl groups on the thermal stability of the trisiloxanylene-m-xylylene polymer versus that of the hybrid fluorosilicone, FCS-210, as well as on that of the fluorosilicone alone.

The thermal stability of poly[1,1,3,3-tetramethyldisiloxanylene-m-xylylene] (18a) was compared to that of poly[tetramethyl-p-silphenylene-siloxane] (21). Other sets of polymers

Figure 5. Thermogravimetric analyses of FCS-210 (curve ▲) and poly[1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]

Heating rate = 5°C/min. in vacuum

with vinyl groups (curve +)

without vinyl groups (curve ⊙)

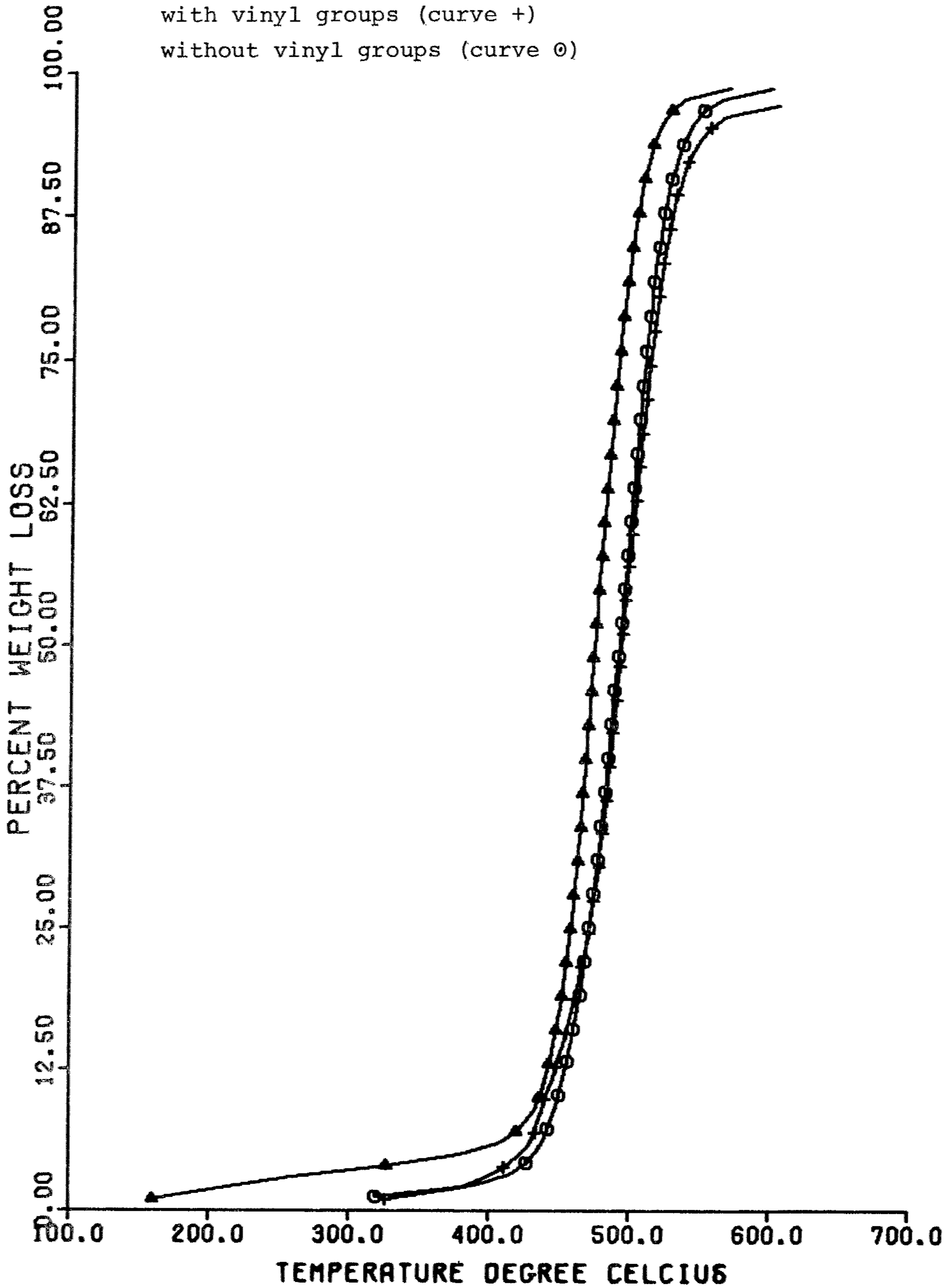
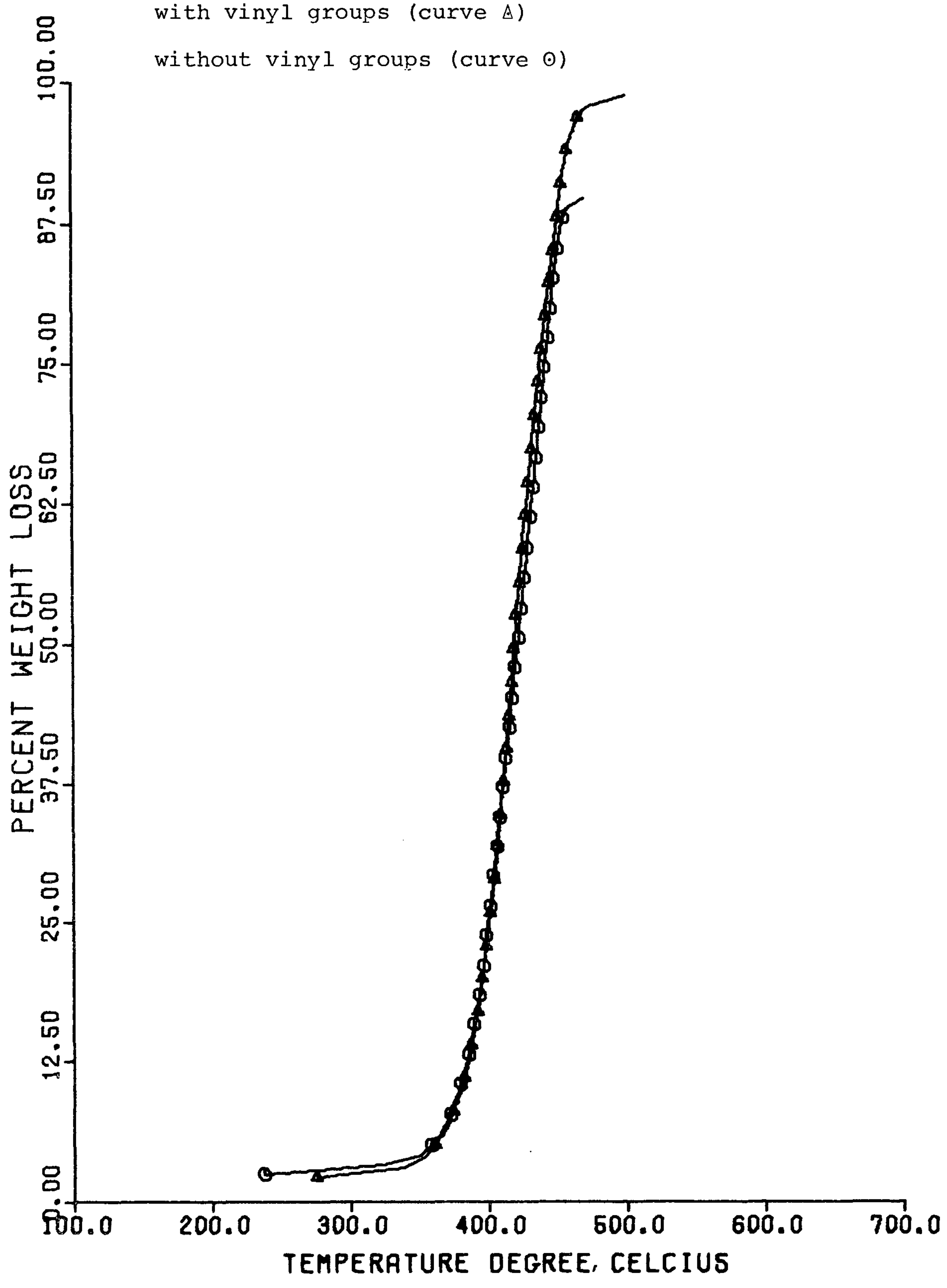


Figure 6. Thermogravimetric analyses of a fluorosilicone with and without vinyl groups

Heating rate = 5°C/min. in vacuum

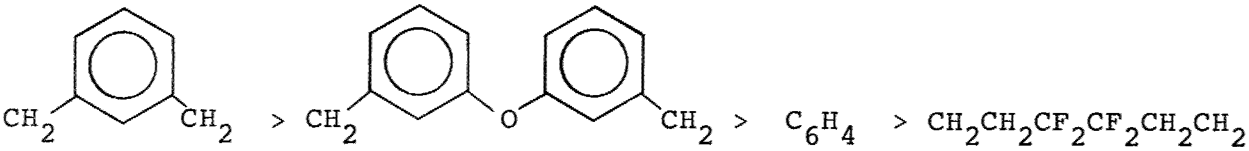
with vinyl groups (curve Δ)

without vinyl groups (curve ⊙)

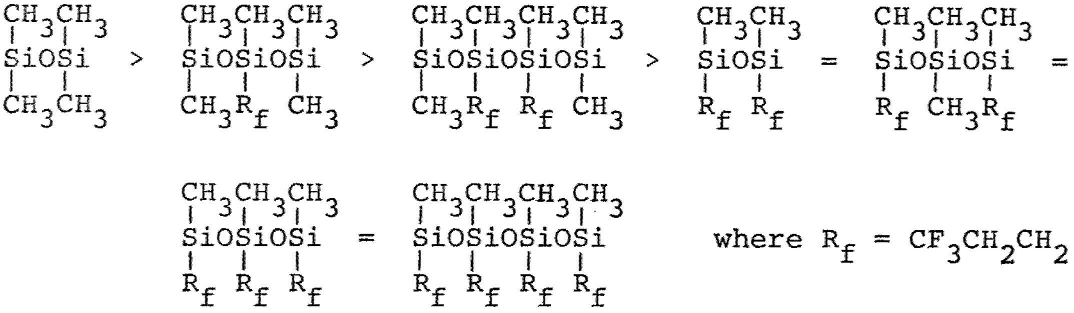


studied included poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene] (19c) versus poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl) trisiloxanylene-m-phenylene] (22), and poly[1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-m-xylylene] (20a) versus poly[1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-p-phenylene] (23). The thermograms for these polymers are shown in Figures 7, 8 and 9. The syntheses of monomers and polymers containing phenylene units are reported elsewhere[9,16] as well as in the next report in this series. In each case, the polymers 18a, 19c and 20a, containing m-xylylene units in the polymer chain, showed superior thermal stabilities to those of the corresponding polymers containing phenylene segments.

The decreasing order of thermal stability of siloxanylene polymers containing aliphatic and aromatic units in the backbones of the polymers is as follows:



The thermal stability of the siloxanylene chains in siloxanylene-m-xylylene polymers decreases in the following order:


$$\begin{matrix}\mathrm{CH_3}&&\mathrm{CH_3}\\|&&|\\\mathrm{Si}&\mathrm{O}&\mathrm{Si}\\|&&|\\\mathrm{CH_3}&&\mathrm{CH_3}\end{matrix} > \begin{matrix}\mathrm{CH_3}&&\mathrm{CH_3}&&\mathrm{CH_3}\\|&&|&&|\\\mathrm{Si}&\mathrm{O}&\mathrm{Si}&\mathrm{O}&\mathrm{Si}\\|&&|&&|\\\mathrm{CH_3}&&\mathrm{R_f}&&\mathrm{CH_3}\end{matrix} > \begin{matrix}\mathrm{CH_3}&&\mathrm{CH_3}&&\mathrm{CH_3}&&\mathrm{CH_3}\\|&&|&&|&&|\\\mathrm{Si}&\mathrm{O}&\mathrm{Si}&\mathrm{O}&\mathrm{Si}&\mathrm{O}&\mathrm{Si}\\|&&|&&|&&|\\\mathrm{CH_3}&&\mathrm{R_f}&&\mathrm{R_f}&&\mathrm{CH_3}\end{matrix} > \begin{matrix}\mathrm{CH_3}&&\mathrm{CH_3}\\|&&|\\\mathrm{Si}&\mathrm{O}&\mathrm{Si}\\|&&|\\\mathrm{R_f}&&\mathrm{R_f}\end{matrix} = \begin{matrix}\mathrm{CH_3}&&\mathrm{CH_3}&&\mathrm{CH_3}\\|&&|&&|\\\mathrm{Si}&\mathrm{O}&\mathrm{Si}&\mathrm{O}&\mathrm{Si}\\|&&|&&|\\\mathrm{R_f}&&\mathrm{CH_3}&&\mathrm{R_f}\end{matrix} =$$

$$\begin{matrix}\mathrm{CH_3}&&\mathrm{CH_3}&&\mathrm{CH_3}\\|&&|&&|\\\mathrm{Si}&\mathrm{O}&\mathrm{Si}&\mathrm{O}&\mathrm{Si}\\|&&|&&|\\\mathrm{R_f}&&\mathrm{R_f}&&\mathrm{R_f}\end{matrix} = \begin{matrix}\mathrm{CH_3}&&\mathrm{CH_3}&&\mathrm{CH_3}&&\mathrm{CH_3}\\|&&|&&|&&|\\\mathrm{Si}&\mathrm{O}&\mathrm{Si}&\mathrm{O}&\mathrm{Si}&\mathrm{O}&\mathrm{Si}\\|&&|&&|&&|\\\mathrm{R_f}&&\mathrm{R_f}&&\mathrm{R_f}&&\mathrm{R_f}\end{matrix}$$

where $R_f = CF_3CH_2CH_2$

The glass-transition temperatures of the poly[siloxanylene-m-xylylene] synthesized as well as those of related polymers

Figure 7. Thermogravimetric analyses of poly[1,1,3,3-tetramethyldisiloxanylene-m-xylylene] (curve O) and poly[tetramethyl-p-silphenylene-siloxane] (curve Δ)

Heating rate = 5°C/min. in vacuum

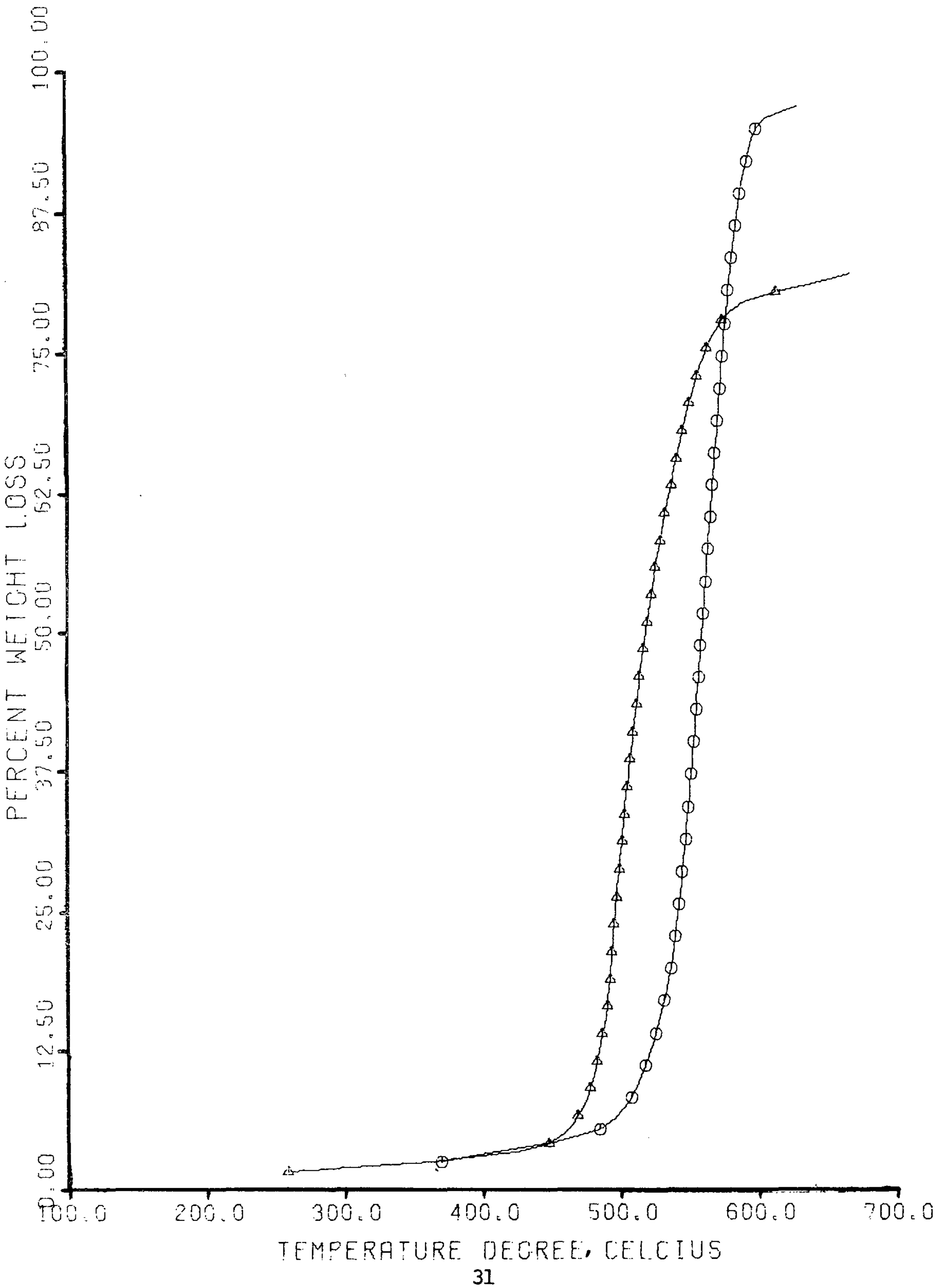


Figure 8. Thermogravimetric analyses of poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene] (curve ⊙) and poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)trisiloxanylene-m-phenylene] (curve Δ)

Heating rate = 5°C/min. in vacuum

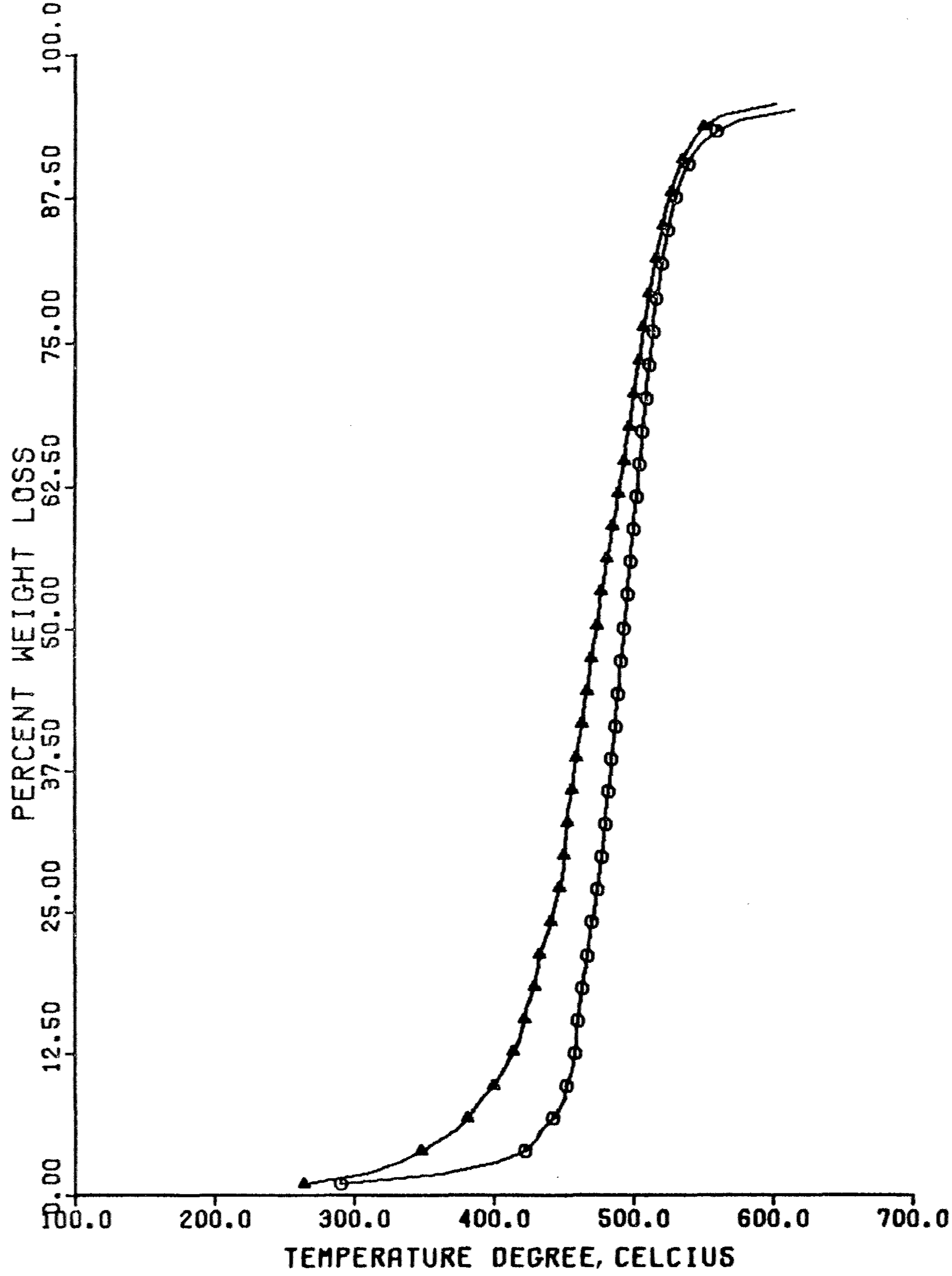
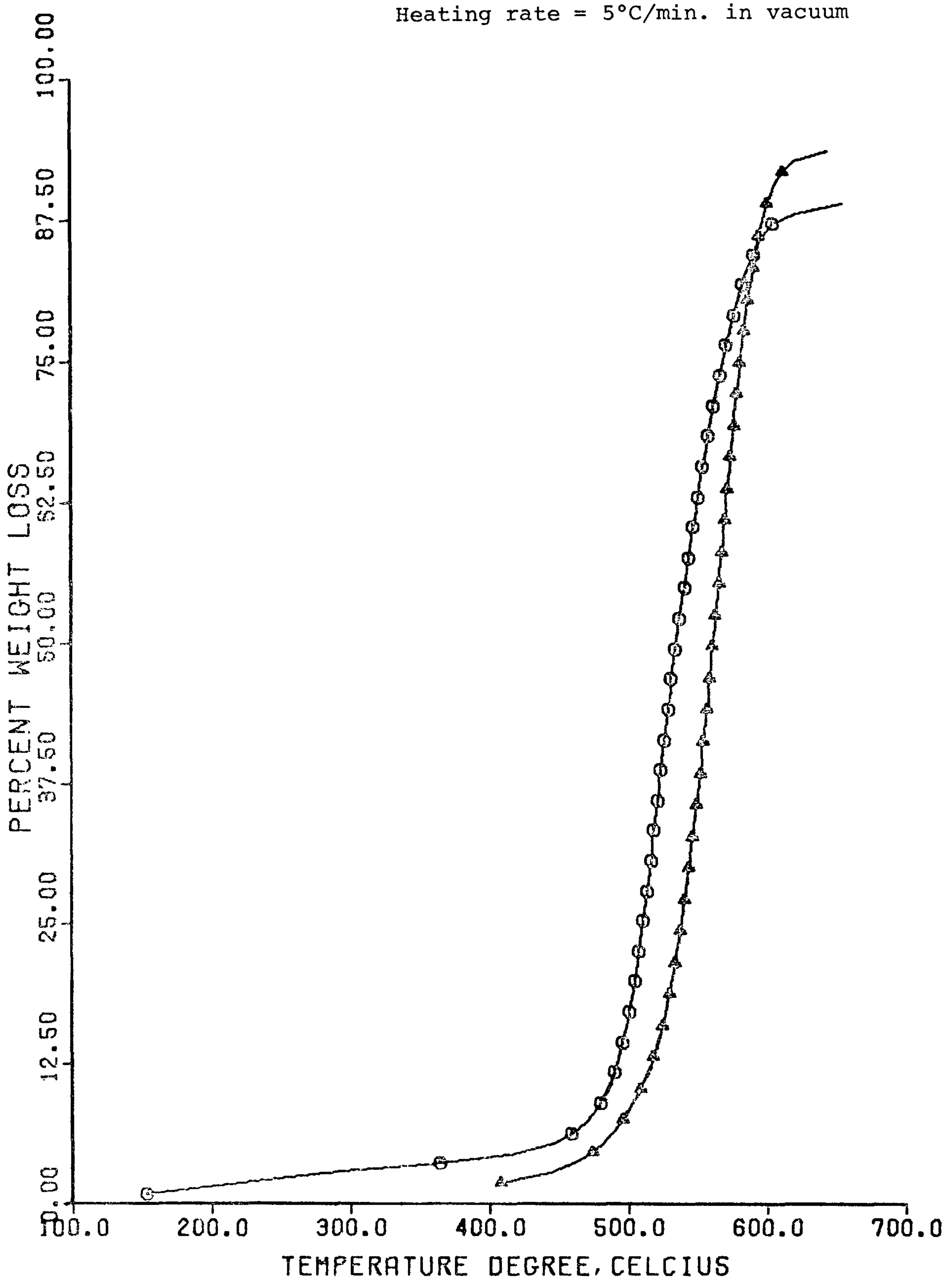


Figure 9. Thermogravimetric analyses of poly[1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-m-xylylene] (curve Δ) and poly[1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-p-phenylene] (curve O)



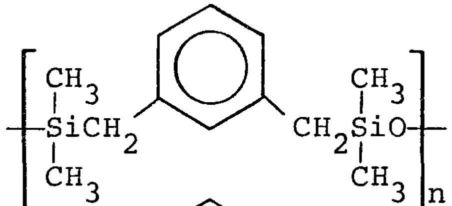
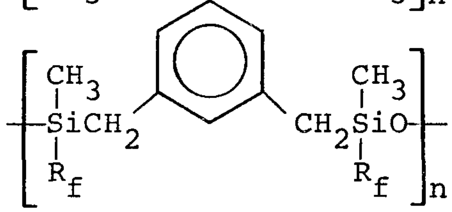
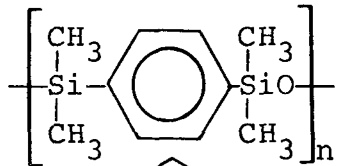
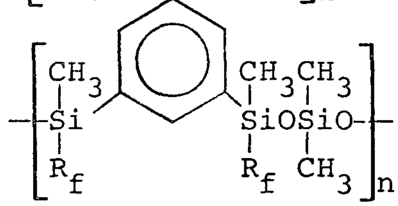
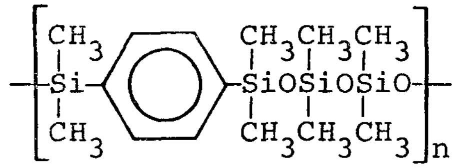
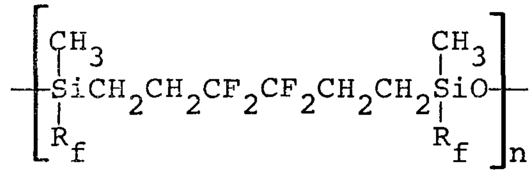
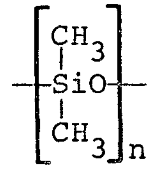
were determined by differential scanning calorimetry (DSC) at a heating rate of 20° per minute. The glass-transition temperatures obtained for these polymers are listed in Tables III, IV and V, along with the results recorded for the other polymers of interest.

The glass-transition temperature of poly[tetramethyl-p-silphenylene-siloxane] (21) has been reported to be -23°,[16] which is considered to be too high for application in the formulation of aircraft fuel tank sealants or other broad-temperature range elastomers. Therefore, in investigating such arylenesiloxanylene polymers, it was desired to lower the Tg of the polymer by incorporation of methylene bridges between the phenylene moiety and the silicon atoms. The m-phenylene moiety was selected for the arylene segment because it was expected to provide a slightly lower Tg than does p-phenylene. Incorporation of methylene bridges between the m-phenylene and tetramethyldisiloxanylene units, polymer 18a, resulted in a considerable reduction (of 18 degrees) in Tg, from that of polymer 21. However, the substitution of two 3,3,3-trifluoropropyl groups for methyls in poly(1,1,3,3-tetramethyldisiloxanylene-m-xylylene) (18a) resulted in raising the glass-transition temperature of polymer 18b to -19° from -41°. Polymer 18c, containing methylene-3,3′-oxydiphenylenemethylene units, exhibited a glass-transition temperature of -18°. The incorporation of this unit into the siloxanylene chain did not provide a reduction in the glass-transition temperature of the polymer when compared to the corresponding polymer with m-phenylene units. Therefore, further research on the latter type of polymer containing oxydiphenylene units was minimized.

The results obtained in determination of the glass-transition temperatures of the poly[trisiloxanylene-m-xylylenes] and poly[tetrasiloxanylene-m-xylylenes] indicated that the addition of one dimethylsiloxane unit to the siloxanylene segment decreased the glass-transition temperature by 15°, whereas the substitution of one 3,3,3-trifluoropropyl for one methyl group increased the glass-transition temperature by 8-10°.

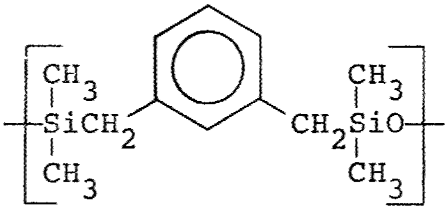
Table V

Physical and Thermal Properties of Poly[disiloxanylene-*m*-xylylenes] and Other Related Polymers of Interest

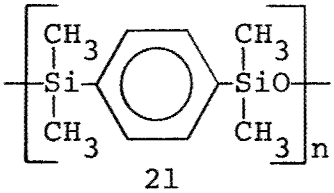
Polymer	[η] dl/g, 30°	Molecular Weight, $\bar{M}_n$	Tg, °C	°C at % TGA Weight Loss 10%	25%	50%
	0.46	38,880	-41	513	541	559
			-19	436	461	482
	1.35 (inh) (THF)	55,100	-23	479	496	519
			-46	401	443	474
			-81	484	511	536
 $\left[\overset{CH_3}{\underset{R_f}{Si}}CH_2CH_2CF_2CF_2CH_2CH_2\overset{CH_3}{\underset{R_f}{Si}}O\right]_n$ + 3% Vinyl			-26	436	458	474
 $\left[\overset{CH_3}{\underset{CH_3}{Si}}O\right]_n$		172,528	-125	424	453	488

The substitution of 3% vinyl for 3,3,3-trifluoropropyl groups resulted in insignificant change in the glass-transition temperature.

As already noted, when two methylene moieties were incorporated between the benzene ring and the disiloxanylene linkage of an arylenesiloxanylene polymer such as poly(1,1,3,3-tetramethyl-*p*-silphenylene-siloxane), polymer 21, a dramatic reduction in the glass-transition temperature was observed for the resulting polymer, poly[1,1,3,3-tetramethyldisiloxanylene-*m*-xylylene], 18a. However, the dramatic effect of introduction of methylene units on the glass-transition temperatures disappeared in the polymers with longer siloxanylene linkages, such as the trisiloxanylene or tetrasiloxanylene unit. The polymers 19c and 20a, containing *m*-xylylene and trisiloxanylene or tetrasiloxanylene moities, exhibited slightly higher glass-transition temperatures than those of the corresponding polymers, 22 and 23, containing phenylene instead of *m*-xylylene units.


18a

vs.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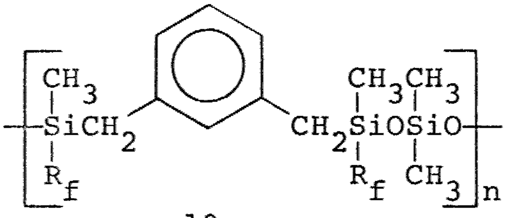
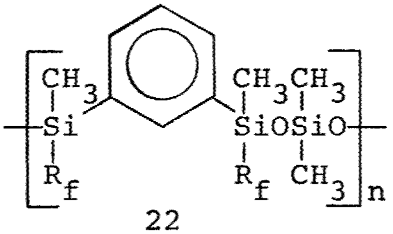

19c

vs.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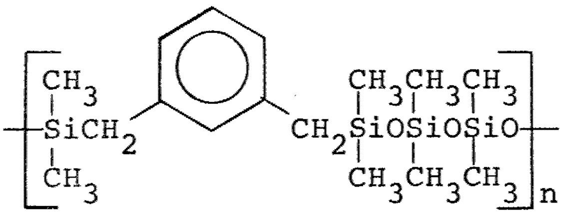
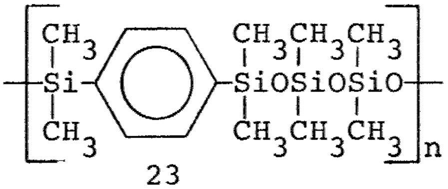
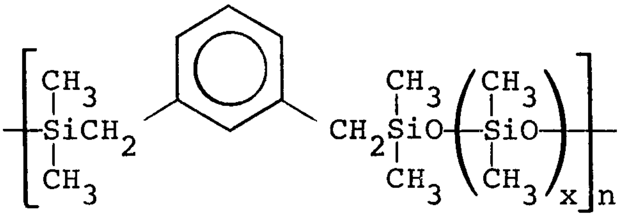

20a

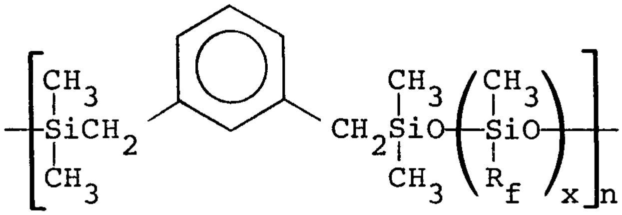
vs.

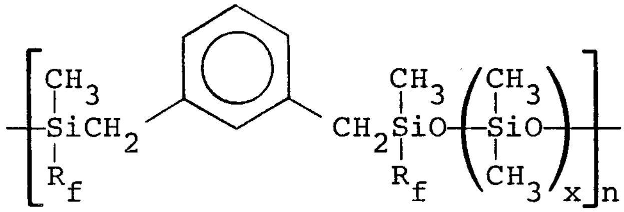

23

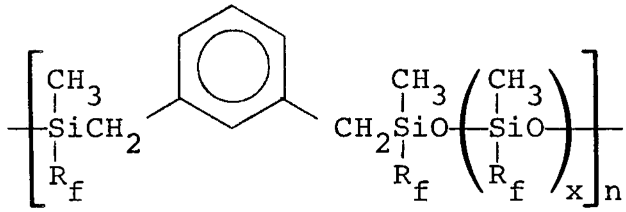
$R_f = CF_3CH_2CH_2$

The relationships between the glass-transition temperature and polymer composition for the following polymer series are shown in Figures 10 and 11.





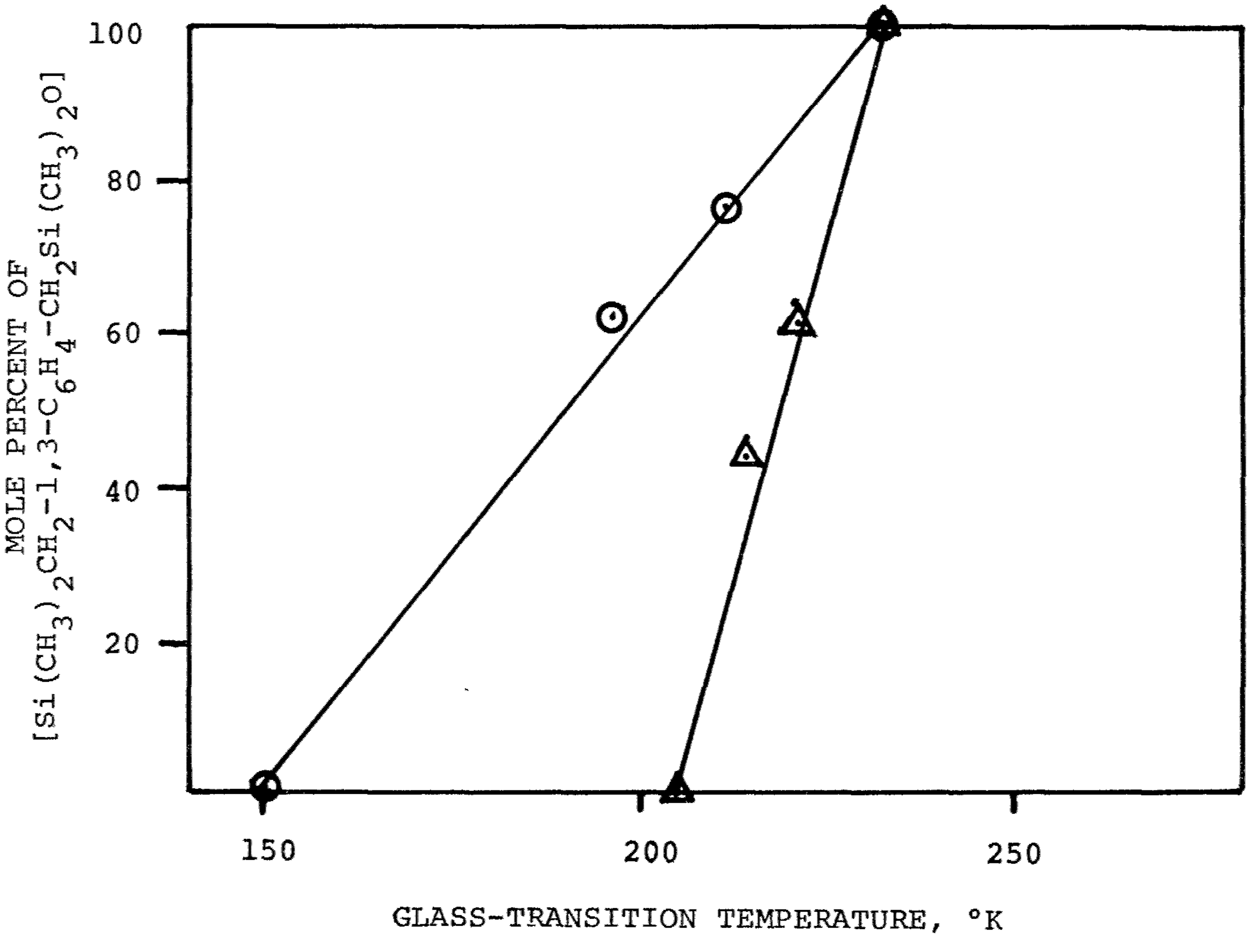


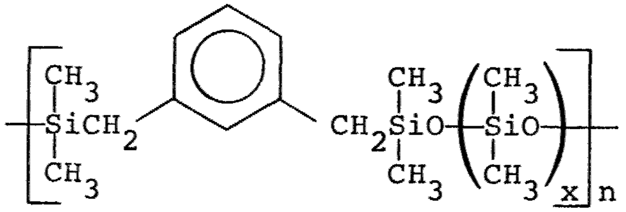


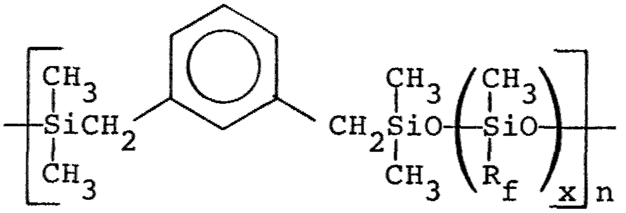
D. Properties of Vulcanizates

The synthesized alkarylenesiloxanylene polymers described in this report were successfully cured without difficulty using two parts per hundred of an organic diperoxide, di-t-butyl dicumyl peroxide (Vulcup R - trade mark of Hercules, Inc.). The facile crosslinking of alkarylenesiloxanylene polymers made it possible to evaluate the properties of cured polymers, in terms of their resistance to solvents (including advanced jet fuels), tensile

Figure 10. Relationship between Tg and Polymer Composition in Poly(siloxanylene-m-xylylenes) - A

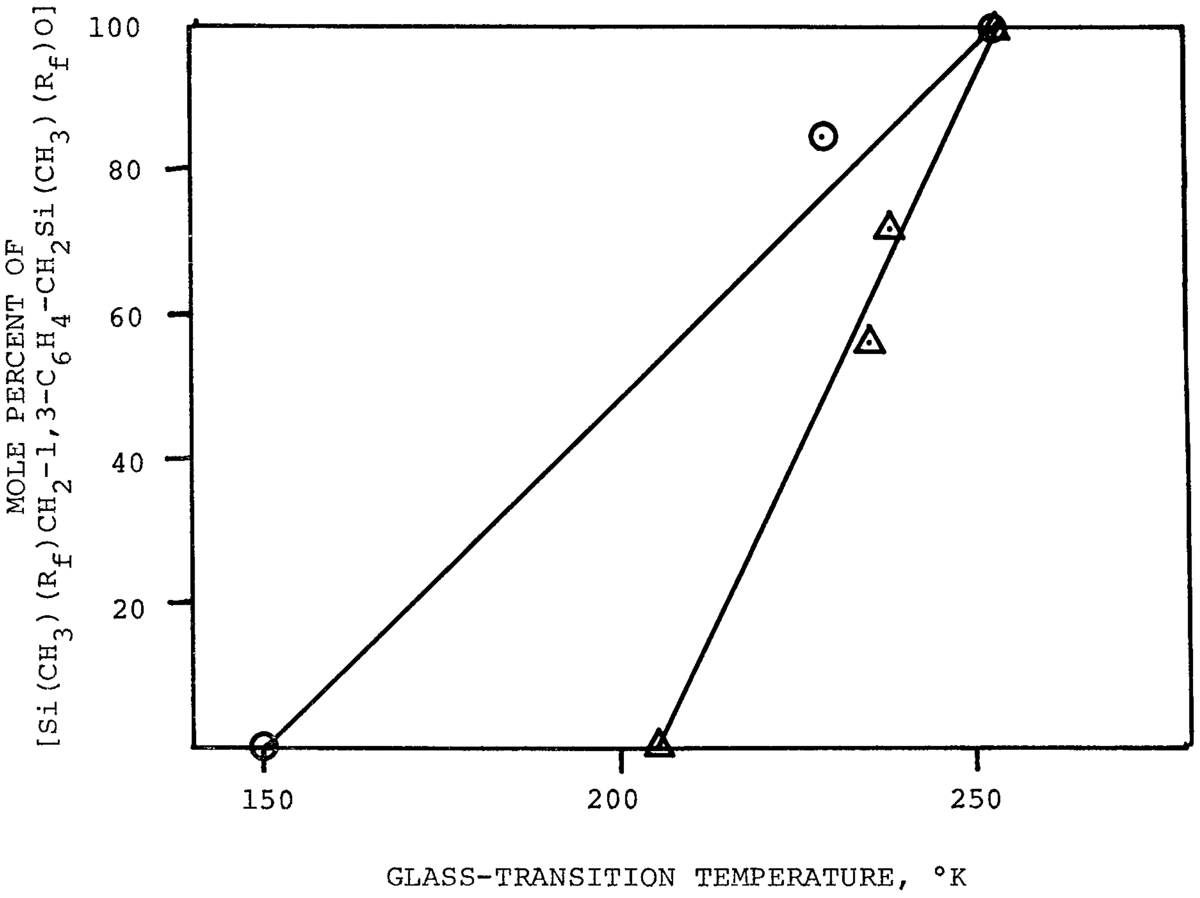


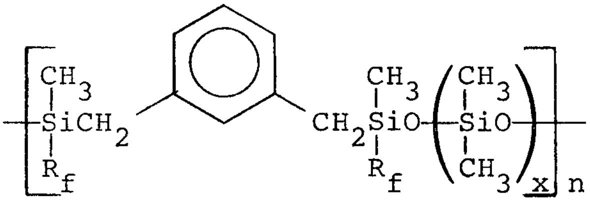

(curve ⊙)


(curve ⚠)

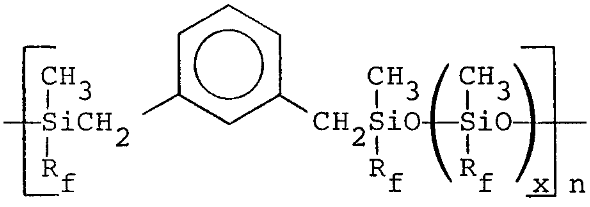
$R_f = CF_3CH_2CH_2$

Figure 11. Relationship between Tg and Polymer Composition in Poly(siloxanylene-m-xylylenes) - B





(curve ⊙)



(curve ▵)

$R_f = CF_3CH_2CH_2$

properties, Shore A hardness, and resistance to reversion in a confined thermal environment.

Initial samples of polymers were cured in a Teflon mold without a top with heating at 190° and one atmosphere for one hour. Under these conditions, the surface of the polymer remained uncured, probably due to the inhibition of free radical reaction in the presence of oxygen. The uncured surface was washed and removed with n-hexane to obtain the test specimen. Polymers were also cured completely (throughout the sample specimens) by compression-molding for 30 minutes at 170° and 2000 psi. using a stainless steel mold with a Teflon cover. The vulcanizates were post-cured for 16 hours at 120° and 0.1 Torr.

The vulcanizates were used to determine the resistance to swell by solvents, such as iso-octane and JP-4 jet fuel, at room temperature. Results of the swell tests are summarized in Tables VI and VII. Plots of the change in volume of elastomers after immersion in JP-4 or iso-octane for 72 hours at ambient temperature versus percent fluorine content of the polymer for the two series of polymers containing tri- and tetrasiloxanylene linkages, are shown in Figures 12 and 13. An analysis of results indicated that approximately 30% of fluorine content, based on the polymer weight, is required to provide polymers with an adequate resistance to solvent attack, i.e., to keep the swell ratio under a desired 10%.

The elastomers obtained by curing polymers 18a, 18b, 19d, 20a, 20b, 20c, FCS-210 and FCS-810 showed excellent resistance to reversion after heating for 24 hours at 260° in a confined thermal environment.

Table VI

Fuel Resistance of Siloxanylene-*m*-xylylene and Related Elastomers Cured Under Atmospheric Pressure at 190° for 1 Hour

Polymer	% Fluorine	Volume Swell Ratio 72 Hrs. at RT	
		JP-4	Iso-octane
18a	0	189	105
18b		0	7
19a	0	76	56
19b	14.5	50	24
19c		5	12.5
19d	30.7	1.5	6
FCS-210	42	5.8	36
FCS-810		0	14

Table VII

Fuel Resistance of Siloxanylene-*m*-xylylene and Related Elastomers Cured Under a Pressure of 2000 psi at 170° for 30 Minutes

Polymer	% Fluorine	Volume Swell Ratio 72 Hrs. at RT JP-4	 Iso-octane
19a	0	200	221
19b	14.5	166	145
19d	30.7	7.6	11
19e		24.2	27.7
20a	0	150	170
20b	21	77	60.5
20c	32	4.5	0
FCS-210	42	14.1	18
LS Homopolymer	36.5	5.7	7
LS-420	36.5	4.2	11
LS/FCS-210 0.9/1 Random	40.6	0	12.5

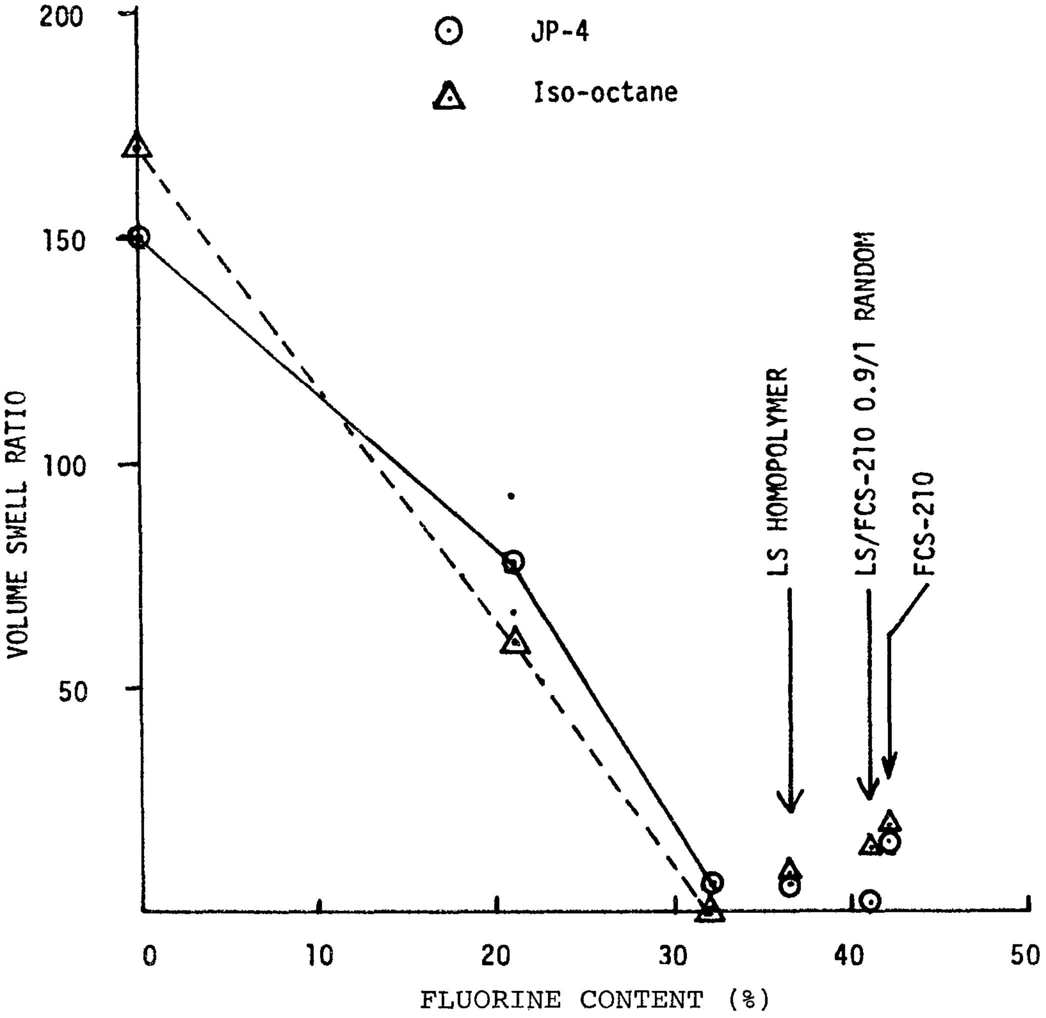


Figure 12. Volume Swell Ratio Versus Percent Fluorine Content of Poly[trisiloxanylene-m-xylylenes], 19a, 19b and 19d

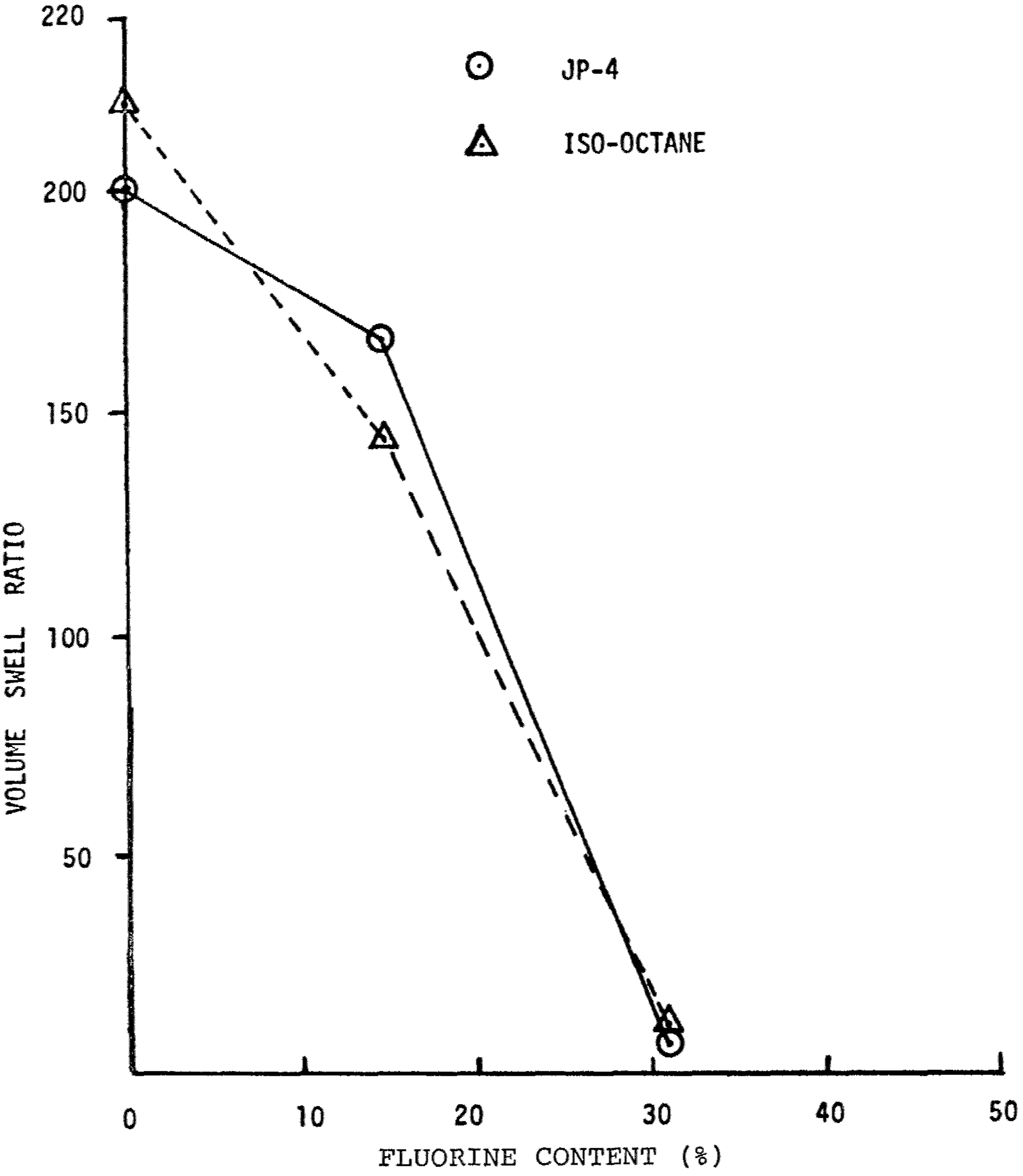


Figure 13. Volume Swell Ratio Versus Percent Fluorine Content of Cured Poly[tetrasiloxanylene-m-xylylenes], 20a, 20b and 20c, and Related Polymers of Interest

SECTION III
EXPERIMENTAL

A. General

All melting points reported are uncorrected. Molecular weights were determined by vapor phase osmometry (VPO) or by membrane osmometry (MO) unless stated otherwise. Elemental analyses were carried out by the Analytical Branch, Electromagnetic Materials Division, Air Force Materials Laboratory. Nuclear magnetic resonance spectra were obtained on a Varian Model A-60 spectrometer, while infrared spectra were obtained as KBr pellets for solids and by using CsI or NaCl plates for liquids on either a Perken-Elmer Model 21 or a Beckmann Model IR-33 spectrophotometer.

Nuclear magnetic resonance, infrared and mass spectra for the important compounds synthesized are included at the end of the experimental section.

Tetramethylsilane was used as an external standard for proton nmr spectra, while fluorotrichloromethane ($CFCl_3$) was used for fluorine (F^{19}) nmr spectra.

Gas liquid chromatographic analyses were carried out in a Hewlett Packard Model 5750B gas chromatograph by the use of a 6' x 1/8" column packed with Dexil 300 GC (15%), Chromasorb W or 80-100 DMCS, at a programmed heating rate of 10° per minute from 120° to 300°, and at a flow rate of 30 ml. per minute of helium, unless stated otherwise. However, some analytical samples were separated and purified by the use of a 12' x 1/2" column packed with 10% SE-30, 80-100 DMCS, or WHP 5752 at a helium flow rate of 120 ml. per minute.

B. Synthesis of Intermediates, Monomers and Catalysts

1. α,α´-Bis(3,3,3-trifluoropropylmethylchlorosilyl)-m-xylene

To a mixture of magnesium (9.72 g., 0.4 g-atom) and methyl-3,3,3-trifluoropropyldichlorosilane (105.5 g., 0.5 mole) in tetrahydrofuran (100 ml.) was added dropwise under nitrogen a solution of α,α´-dibromo-m-xylene (52.76 g., 0.2 mole) in tetrahydrofuran (100 ml.) over a two-hour period. The addition was controlled to maintain reaction over a temperature range of 50-60°. The resulting mixture was then heated under reflux for 16 hours. After adding 200 ml. of n-hexane to the mixture, the inorganic solids formed were removed by filtration. Fractional distillation of the filtrate gave 42.9 grams (47.2%) of α,α´-bis(3,3,3-trifluoropropylmethylchlorosilyl)-m-xylene: bp 153-154°/0.1 Torr.; mass spec (70 eV), m/e 454 (M^+), 279, and trace of m/e 498 [α-chloromethyl(3,3,3-trifluoropropyl)-α´-bromomethyl-(3,3,3-trifluoropropyl)silyl-m-xylene].

2. α,α´-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

   a. From α,α´-Bis(3,3,3-trifluoropropylmethylchlorosilyl)-m-xylene

A solution of sodium ethoxide, prepared from 2.83 grams of sodium and 200 ml. of absolute ethanol, was added slowly under nitrogen to 28 grams (0.0617 moles) of α,α´-bis(3,3,3-trifluoropropylmethylchlorosilyl)-m-xylene. The reaction mixture was heated under reflux for 15 minutes and then cooled to room temperature. Ethanol was removed by evaporation on a rotary evaporator to leave a residue which was transferred into a smaller flask eith the aid of diethyl ether. Fractional distillation of the residue gave 17.7 grams (59.5%) of α,α´-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene: bp 140-141°/0.03 Torr or 153-155°/0.5 Torr.

   b. From Ethoxymethyl-3,3,3-trifluoropropylchlorosilane

To a mixture of magnesium (7.29 g., 0.3 g-atom) and ethoxymethyl-3,3,3-trifluoropropylchlorosilane (99 g., 0.45 moles, 90% purity) in 200 ml. of tetrahydrofuran ws added 35 ml. of a solution of α,α´-dibromo-m-xylene (39.6 g., 0.15 moles) in 200 ml. of tetrahydrofuran at one time. After the Grignard reagent started to form, the rest of the dibromide solution was added dropwise into the flask over a period of two hours. The reaction temperature was controlled with a water bath to maintain the reaction temperature at 35°. The reaction mixture was stirred for 16 hours at room temperature and, after adding 200 ml. of n-hexane, the inorganic salts formed were removed by filtration. Fractional distillation of the filtrate yielded the solvents and 40.7 grams of a mixture (40:60) of ethoxymethyl-3,3,3-trifluoropropylchlorosilane and diethoxymethyl-3,3,3-trifluoropropylsilane: bp 42-50°/5 Torr. The residue from this distillation was treated with 10 ml. of absolute ethanol and the additional inorganic salts formed were removed again by filtration. Distillation of the filtrate gave 6.3 grams (8.8%) of α,α´-bis(ethoxymethyl-3,3,3-trifluoropropylsilyl)-m-xylene: bp 149.5-152°/0.05 Torr. The GLC chromatogram and infrared spectrum were identical with that of an authentic sample prepared by an alternate route.

c. From α,α´-Bis(methyl-3,3,3-trifluoropropylsilyl)-m-xylene

To a solution of sodium ethoxide, prepared from 0.55 gram of sodium and 15 ml. of absolute ethanol, was added 3.09 grams of α,α´-bis(methyl-3,3,3-trifluoropropylsilyl)-m-xylene over a period of 10 minutes at room temperature. Evolution of hydrogen ceased after 10 minutes and the solvent was removed by evaporation on a rotary evaporator. Fractional distillation of the residue gave 0.6 gram of crude α-[ethoxymethyl(3,3,3-trifluoropropyl)-silyl]-m-xylene boiling at 95-105°/0.04 Torr and 0.3 gram (7.9%) of crude α,α´-bis(ethoxymethyl-3,3,3-trifluoropropylsilyl)-m-xylene, boiling at 115-117°/0.04 Torr. Analytical samples of α,α´-bis-[ethoxymethyl(3,3,3-trifluoropropyl)silyl-m-xylene and α-[ethoxymethyl(3,3,3-trifluoropropyl)silyl-m-xylene were obtained by purification of the crude products using a preparative GLC. Calcd for $C_{20}H_{32}Si_2F_6O_2$: C, 49.78; H, 6.68. Found: C, 49.89; H, 7.04. Calcd for $C_{14}H_{21}F_3OSi$: C, 57.12; H, 7.19. Found: C, 55.22; H, 7.10.

3. α,α´-Bis[hydroxymethyl-(3,3,3-trifluoropropyl)silyl]-m-xylene

To a stirred mixture of 8 grams of sodium hydroxide, 34 ml. of methanol and 3.7 ml. of water, was added 23 grams of α,α´-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene, followed by the addition of a solution of 8 grams of sodium hydroxide and 37 ml. of water. The resulting mixture was stirred for 30 minutes, and then poured into a solution of 50 grams of potassium dihydrogen phosphate in 970 grams of water and ice. Ether was used to extract the oily product and the ether extract was washed with water, dried over anhydrous magnesium sulfate and the ether removed by evaporation on a rotary evaporator. Fractional distillation of the clear oily residue through a short path distillation column gave 14.4 grams (71%) of the desired product, α,α´-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene: bp 168-169°/0.12 Torr; nmr (CCl_4, external TMS) δ -0.0667 (s, 6, $SiCH_3$), 0.5-1 (m, 4, $SiCH_2$), 1.5-2.33 (m, 8, CH_2 and $SiCH_2C_6H_4$), 3.9 (s, 2, OH) and 6.34-7.25 (m, 4, ArH); F^{19} nmr (CCl_4, external $CFCl_3$) -3860 Hz. (t, CF_3); mass spec (290 eV) m/e 418 and 227; molecular weight (benzene, VPO) 419, 427 (theory 418). Calcd for $C_{16}H_{24}F_6O_2Si_2$: C, 45.92; H, 5.78. Found: C, 46.09; H, 6.05.

4. Diethoxymethyl(3,3,3-trifluoropropyl)silane

In a 100-ml. three-necked flask equipped with a thermometer, stirrer, addition funnel connected to a nitrogen supply, and a Friedrich condenser connected to another flask containing pyridine (30 g.) and an outlet leading to a gas-trap, was placed 21.1 grams (0.1 mole) of 3,3,3-trifluoropropylmethyldichlorosilane. Absolute ethanol (10.12 g., 0.22 mole) was added slowly into the flask over a 30-minute period and the hydrochloric acid gas evolved was absorbed over pyridine. The resulting mixture was stirred for 18 hours at room temperature, after which GLC analysis of the mixture indicated that it consisted of 3,3,3-trifluoropropylmethyldichlorosilane (0.043%), 3,3,3-trifluoropropylmethylethoxychlorosilane (11.8%), and 88.2% of the desired diethoxysilane. An additional 6 grams of absolute ethanol was then added to the mixture in order to convert the monoethoxy derivative to the diethoxysilane. The reaction mixture was kept at 80-90° for 4.5 hours until the GLC peak for the monoethoxy derivative disappeared. The mixture was then fractionated on a spinning-band column to yield 13.8 grams (62.3%) of diethoxymethyl-3,3,3-trifluoropropylsilane: bp 151-152.5°: nmr (external TMS), δ 0 (s, 3, $SiCH_3$), 0.4-0.8 (m, 2, $SiCH_2$), 1.1 (t, 6, CCH_3), 1.5-2.4 (m, 2, CF_3CH_2) and 3.6 (q, 4, OCH_2); F^{19} nmr ($CFCl_3$) δ -70.2 (t, CF_3); mass spec (70 eV), m/e 182 for $M-C_2H_5F^+$. Calcd for $C_8H_{17}F_3O_2Si$: C, 41.72; H, 7.44; F, 24.75; Si, 12.20. Found: C, 41.90; H, 7.31; F, 24.98; Si, 11.72.

5. 3,3,3-Trifluoropropylethoxymethylchlorosilane

3,3,3-Trifluoropropylmethyldichlorosilane (42.2 g., 0.2 mole) was reacted with 9.2 grams (0.2 mole) of absolute ethanol, using the procedure described for the preparation of 3,3,3-trifluoropropyldiethoxymethylsilane except that the reaction was stopped after 18 hours of stirring at room temperature. GLC analysis of the mixture indicated that it consisted of 6% of 3,3,3-trifluoropropylmethyldichlorosilane, 88.4% of 3,3,3-trifluoropropylmethylethoxysilane and 5.6% 3,3,3-trifluoropropyldiethoxymethylsilane. Fractional distillation of this mixture through a spinning-band column gave 30.8 grams of crude 3,3,3-trifluoropropylethoxymethylchlorosilane of about 90% purity: bp 136-139.5°. An analytical sample was obtained by purification of this mixture by means of a preparative GLC column. Mass spectral analysis showed m/e 175 for $M-OC_2H_5^+$. Calcd for $C_6H_{12}F_3OSiCl$: C, 32.65; H, 5.48; Cl, 16.06; F, 25.83; Si, 12.73. Found: C, 32.75; H, 5.81; Cl, 18.70; F, 24.75; Si, 12.96.

6. α,α′-Bis(methylchlorosilyl)-*m*-xylene

α,α′-Bis(methylchlorosilyl)-*m*-xylene was prepared from 52.76 grams (0.2 mole) of α,α′-dibromo-*m*-xylene, 92 grams (0.8 mole) of methyldichlorosilane and 9.72 grams of magnesium, using the same procedure as described for the preparation of α,α′-bis-(3,3,3-trifluoropropylmethylchlorosilyl)-*m*-xylene. Two fractional distillations of the crude product through a spinning-band column gave 6 grams of α,α′-bis(methylchlorosilyl)-*m*-xylene: bp 102-102.5°/0.1 Torr or 95°/0.07 Torr; nmr δ 0 (d, 6, $SiCH_3$), 2.0 (d, 4, CH_2), 4.4 (m, SiH) and 6.3-6.8 (m, 4, ArH); mass spec (70 eV), m/e 262.0161 (theory 262.0167).

7. α,α′-Bis(3,3,3-trifluoropropylmethylsilyl)-m-xylene

a. From α,α′-Bis(3,3,3-trifluoropropylmethylchlorosilyl)-m-xylene

Twenty milliliters of a 0.95 mole solution of lithium aluminum hydride in tetrahydrofuran was added dropwise under nitrogen into a solution of one gram of α,α′-bis[3,3,3-trifluoropropylmethylchlorosilyl]-m-xylene in tetrahydrofuran. After the mixture was heated under reflux for one hour, the excess lithium aluminum hydride was decomposed with water and ice. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed by evaporation on a rotary evaporator to leave a clear liquid. Distillation of the liquid gave 0.7 gram (82.5%) of α,α′-bis(3,3,3-trifluoropropylmethylsilyl)-m-xylene: bp 108°/0.15 Torr.

b. From α,α′-Bis(methylchlorosilyl)-m-xylene

To a stirred mixture of α,α′-bis(methylchlorosilyl)-m-xylene (5.24 g., 0.02 mole) and 1.22 grams (0.05 g-atom) of magnesium in 50 ml. of tetrahydrofuran in a flask which was cooled by an ice-water bath, was added dropwise under nitrogen 7.8 grams (0.44 mole) of 1-bromo-3,3,3-trifluoropropylpropane. The reaction temperature was kept at 0-7° during the addition and was then stirred for 8 hours at 0-3°. The mixture was allowed to warm up to room temperature during the next 16 hours, was hydrolyzed with water and then extracted with diethyl ether. The ether extract was dried over anhydrous calcium sulfate and the ether was removed by evaporation to leave a liquid residue (6.5 grams). Distillation of the residue gave 1.2 grams of a fraction boiling at 95-106°/0.15 Torr, 1.8 grams of a second fraction boiling at 107-117°/0.15 Torr, and 0.6 gram of a third fraction boiling at 117-119°/0.15 Torr. A preparative GLC separation of the last fraction provided 0.3 gram of pure α,α′-bis(3,3,3-trifluoropropylmethylsilyl)-m-xylene: Calcd for $C_{16}H_{24}F_6Si_2$: C, 49.72; H, 6.26; F, 29.49; Si, 14.53. Found: C, 49.88; H, 6.33; F, 30.61; Si, 15.10. Mass spectral analysis showed the molecular ion at 386.1335 (theory 386.1320).

8. 3,3,3-Trifluoropropylmethylsilane

To a mixture of 11.4 grams (0.3 mole) of lithium aluminum hydride and 100 ml. of n-butyl ether was added 31.6 grams (0.15 mole) of 3,3,3-trifluoropropylmethyldichlorosilane over a period of 15 minutes during which time the reaction temperature rose from 45 to 95°. Distillation of the mixture gave 13 grams of a mixture of 3,3,3-trifluoropropylmethylsilane (77.7%) and n-butyl ether (22.3%) with boiling point range of 62-67°. Fractional distillation of the mixture provided 9.6 grams (44.8%) of pure 3,3,3-trifluoropropylmethylsilane: bp 58-60° (Lit. bp 58.2°); mass spec (290 eV) m/e 142; mass spec (70 eV) m/e 141 for M^+-H; nmr (from C_6H_6) δ 7.1 upfield (t, 3, $SiCH_3$), 6.1-6.6 upfield (m, 2, $SiCH_2$) 4.8-5.6 upfield (m, 2, CCH_2) and 3.5 upfield (m, 2, SiH); F^{19} nmr (external $CFCl_3$) δ 69.2 (t, CF_3). Calcd for $C_4H_9F_3Si$: C, 33.79; H, 6.38; F, 40.08; Si, 19.75. Found: C, 34.40; H, 6.48; F, 40.02; Si, 20.31.

9. 3,3,3-Trifluoropropylmethylchlorosilane

a. From 3,3,3-Trifluoropropylmethylsilane

A mixture of 2.84 grams (0.02 mole) of 3,3,3-trifluoropropylmethylsilane and 1.43 grams (0.01 mole) of silver chloride was stirred under nitrogen at room temperature for 6.5 hours. Distillation of the reaction product gave 1.5 grams of crude 3,3,3-trifluoropropylmethylchlorosilane, bp 95.5-97° (Lit. bp 96.5°). GLC analysis of the crude product showed a composition of 10.7 : 87.8 : 1.73% of 3,3,3-trifluoropropylmethylsilane: 3,3,3-trifluoropropylmethylchlorosilane: 3,3,3-trifluoropropylmethyldichlorosilane. The desired product was purified by preparative GLC, and its infrared spectrum was found to be identical with that of an authentic sample prepared by another route. Calcd for $C_4H_8ClF_3Si$: C, 27.20; H, 4.57. Found: C, 27.17; H, 4.69. Mass spec (70 eV) m/e 175 and 177 for $M-H^+$ and m/e 141 for $M-Cl^+$; nmr δ 0 (d, 3, 1 $SiCH_3$), 0.384-0.75 (m, 2, $SiCH_2$), 1.25-2.08 (m, 2, CCH_2) and 4.28 (m, 1, SiH). Mass spectral analysis by chemical ionization (290 eV) showed the molecular ion peaks at 176 and 178.

b. From 1-Chloro-3,3,3-trifluoropropane

To a stirred mixture of 23 grams (0.2 mole) of methyldichlorosilane and 2.6 grams (0.11 g-atom) of magnesium in diethyl ether (30 ml.), was added under nitrogen a solution of 13.25 grams (0.1 mole) of 1-chloro-3,3,3-trifluoropropane in 50 ml. of diethyl ether. The resulting mixture was allowed to stir at room temperature for 23 hours during which time the solution turned milky. Inorganic solids were removed by filtration and distillation of the filtrate gave 5.5 grams (31.1%) of crude 3,3,3-trifluoropropylmethylchlorosilane: bp 97-102°.

c. From 1-Bromo-3,3,3-trifluoropropane

Into a 250-ml. three-necked flask, equipped with a thermometer, Dry-Ice-isopropanol condenser and dropping funnel, and cooled by an ice-bath, were placed 30 ml. of diethyl ether, 20.7 grams of methyldichlorosilane and 2.43 grams (0.1 g-atom) of magnesium. A solution of 15 grams (0.09 mole) of 1-bromo-3,3,3-trifluoropropane in 50 ml. of diethyl ether was added dropwise into the flask over a period of 30 minutes. The reaction mixture then was stirred for 6 hours at 0° and for an additional 16 hours at room temperature after which inorganic salts were removed by filtration. Fractional distillation of the filtrate provided 7.9 grams of a mixture of 3,3,3-trifluoropropylmethylchlorosilane, 3,3,3-trifluoropropylmethylbromosilane and 1,3-dimethyl-1,3-bis-(3,3,3-trifluoropropyl)disiloxane in a ratio of 7 : 3.5 : 1. These compounds were then separated by preparative GLC, and the three products analyzed. (a) 3,3,3-Trifluoropropylmethylchlorosilane: Calcd for $C_4H_8ClF_3Si$: C, 27.20; H, 4.57. Found: C, 27.02; H, 4.61. (b) 3,3,3-Trifluoropropylmethylbromosilane: Calcd for $C_4H_8F_3BrSi$: C, 21.74; H, 3.65. Found: C, 22.61; H, 3.97. (c) 1,3-Dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane: Calcd for $C_8H_{16}F_6OSi_2$: C, 32.20; H, 5.41. Found: C, 34.47; H, 5.20.

10. 3,3,3-Trifluoropropylmethylbromosilane

A mixture of 2.84 grams (0.02 mole) of 3,3,3-trifluoropropylmethylsilane and 3.6 grams (0.01 mole) of mercuric bromide[3] was heated under nitrogen for 24 hours at 80°. Distillation of the reaction gave 0.2 gram of the starting material, bp 45-47°, and 1.2 grams of crude 3,3,3-trifluoropropylmethylbromosilane, bp ~98°. Purification of the crude product by preparative GLC gave 0.7 gram (15.9%) of pure 3,3,3-trifluoropropylmethylbromosilane: mass spec (70 eV) m/e 219 and 221 for $M-H^+$, and m/e 123 and 125 for $SiCH_3HBr^+$.

11. 1,3-Dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

3,3,3-Trifluoropropylmethylchlorosilane was allowed to hydrolyze for 24 hours in an open air atmosphere. Purification of the product by preparative GLC gave pure 1,3-dimethyl-1,3-bis-(3,3,3-trifluoropropyl)disiloxane: mass spec (70 eV) m/e 201 for $M-CF_3CH_2CH_2^+$; mass spec (290 eV) m/e 298, 137, 119, 159, 157, and 201; nmr δ 0 (d, 6, $SiCH_3$), 0.417-0.834 (m, 4, $SiCH_2$), 1.41-2.25 (m, 4, CCH_2) and 4.42 (m, 2, SiH). Calcd for $C_8H_{16}F_6OSi_2$: C, 32.20; H, 5.41. Found: C, 31.85; H, 5.32.

1,3-Dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane was also prepared similarly from 3,3,3-trifluoropropylmethylbromosilane. All spectral properties obtained for the product were found to be identical with those of the former compound.

12. 1-Bromo-3,3,3-trifluoropropane

To 44.8 grams (0.2) mole of 1-iodo-3,3,3-trifluoropropane in a three-necked flask equipped with a reflux condenser, stirrer and thermometer, was added 36 grams (0.22 mole) of bromine over a period of 15 minutes. The flask was illuminated with a 150-watts tungsten bulb and the reaction temperature rose to 95° and then decreased to 68° during the addition. At the completion of the addition the resulting mixture was refluxed for an additional 10 minutes. Distillation of the mixture gave 39 grams of crude product boiling at 60-65°. After treating the crude product with 50 ml. of a 10% solution of sodium bisulfite, the lower organic layer was separated and distilled to give 25.2 grams (71%) of 1-bromo-3,3,3-trifluoropropane: bp 60-63° (Lit.[2] bp 60.5-62.5°);

mass spec (70 eV) m/e 176 and 178; nmr (TMS) δ 2.7 (m, 2, CF_3CH_2) and 3.4 (m, 2, CH_2Br). Calcd for $C_3H_4BrF_3$: C, 20.36; H, 2.28; Br, 45.15. Found: C, 20.63; H, 2.19; Br, 45.57. The darp purple residue after distillation was found to consist of 36 grams of iodobromide.

13. 1-Chloro-3,3,3-trifluoropropane

Into a 250-ml. three-necked flask, equipped with a Dry-Ice-isopropanol condenser, gas-inlet tube connected to a cylinder of chlorine, stirrer and thermometer, was placed 44.8 grams (0.2 mole) of 1-iodo-3,3,3-trifluoropropane. The reaction flask was illuminated with a 150-watt tungsten light bulb and chlorine was bubbled through the reactant at a slow rate for a period of 30 minutes. During this time the reaction temperature rose to 85° and then decreased to 47°. The reaction mixture was cooled and then distilled to give 23.4 grams of a fraction with a boiling range of 45-52° and a residue which was found to be iodochloride. After treating the fraction with 50 ml. of a 10% solution of sodium bisulfite, the lower organic layer was separated, and distilled to provide 21.5 grams (81.2%) of 1-chloro-3,3,3-trifluoropane: bp 43-46° (Lit.[2] bp 45-46°; mass spec (70 eV) m/e 132 for (M^+), 112 for $(M\text{-}HF)^+$, 77 for $(CF_2 = CHCH_2)^+$ and 49 for $(CH_2Cl)^+$; mass spec (290 eV) m/e 132 and 134 for $(M)^+$, 112 and 114 for $(M\text{-}HF)^+$ and 77; H^1 nmr (TMS) δ 1.92-2.75 (m, 2 CH_2CF_3) and 3.42 (t, 2 CH_2Cl); F^{19} nmr ($CFCl_3$) δ 67.3 (t, CF_3). Calcd for $C_3H_4ClF_3$: C, 27.19; H, 3.04. Found: C, 27.58; H, 3.23.

14. Hydrolysis of α,α′-Bis[chloromethyl(3,3,3-trifluoropropyl)-silyl]-*m*-xylene

a. With Sodium Bicarbonate/Diethyl Ether/Water

To a mixture of 4.2 grams of sodium bicarbonate, 60 ml. of diethyl ether, and 28 grams of water and ice, was added a solution of 4.54 grams (0.01 mole) of α,α′-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-*m*-xylene in 20 ml. of diethyl ether. After the reaction mixture was maintained at 0° for 15 minutes, the organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Removal of the solvent by evaporation on a rotary evaporator gave a clear oil. Elution of this oil through silica gel (Woelm, dry-column grade, activity III/30 mm.) with benzene provided 1.2 grams of 2,4,13,15-tetrasila-2,14-dioxa-2,4,13,15-tetramethyl-2,4,13,15-tetrakis-(3,3,3-trifluoropropyl) [5.5]metacyclophane: mass spec (290 eV) m/e 800, 781, 669, 400 and 137; nmr (CCl_4, external TMS) δ -0.033-0.083 (m, 12, $SiCH_3$), 0.417-2.25 (m, 24, $SiCH_2$, CCH_2) and 6.5-7.2 (m, 8, ArH).

b. With Potassium Dihydrogen Phosphate/Diethyl Ether/Water

A solution of 4.54 grams (0.01 mole) of α,α'-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-m-xylene in 20 ml. of diethyl ether was added to a stirred mixture of 10.3 grams of potassium dihydrogen phosphate, 100 ml. of water, 100 grams of ice and 80 ml. of diethyl ether. The resulting mixture was stirred for 30 minutes after which the organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. The filtrate was evaporated on a rotary evaporator to leave a liquid residue (3.4 grams). An attempt was made to distill this residue at temperatures up to 275° and 0.9 Torr, but no distillate was obtained. Spectral analysis indicated that the product was a cyclic siloxane polymer with a number average molecular weight of 6200 (DP = ~15).

15. 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl-m-xylylene]-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

A solution of 13.62 grams (0.03 mole) of α,α'-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-m-xylene in 75 ml. of diethyl ether was added rapidly into a mixture of 2.4 grams (0.06 mole) of sodium hydroxide, 45 ml. of water and 15 ml. of diethyl ether, with vigorous stirring at 0°. After 10 minutes, the organic layer was separated, washed, dried over anhydrous magnesium sulfate and evaporated to leave 12 grams (97.5%) of crude product as a viscous oil: mass spec (290 eV) m/e 818; nmr (CCl_4, Ext. TMS) δ 0.01665 and 0.0656 (two s, 12, $SiCH_3$), 0.5-1.17 (m, 8, $SiCH_2$), 1.5-2.34 (m, 16, CH_2, $SiCH_2Ar$), 3.38 (s, 1, OH) and 6.5-7.25 (m, 6.8, ArH).

16. 1,3-Bis(dimethylhydroxysilylmethylene-3,3´-oxydiphenylene)-1,1,3,3-tetramethyldisiloxane

In a three-liter three-necked flask, equipped with a mechanical stirrer, dilution head, condenser and a constant-rate addition funnel, were placed 2 liters of methanol and 5.0 grams of sodium hydroxide. The mixture was refluxed under nitrogen and a solution of 39.4 grams of α,α'-bis(dimethylsilyl)-m-tolyl ether in 250 ml. of methanol was added over a period of six hours. The mixture was refluxed for one hour after completion of the addition, cooled, acidified with 6N hydrochloric acid and then extracted with diethyl ether. Removal of the ether by evaporation gave 36.7 grams of a liquid residue which on distillation yielded the following fractions:

Fraction 1:	0.7 grams, bp 120-170°/0.45 Torr
Fraction 2:	4.2 grams, bp 170-180°/0.45 Torr
Fraction 3:	2.6 grams, bp 180-185°/0.45 Torr
Fraction 4:	28.2 grams, residue after heating at 290°/ 0.45 Torr.

Fraction 4 was identified as 1,3-bis(dimethylhydroxysilylmethylene-3,3´-oxydiphenylenemethylene)-1,1,3,3-tetramethyldisiloxane: mass spec (70 eV) 656 and 346; mass spec (290 eV) 674, 656 and 346; molecular weight (benzene, VPO) 660, 665 (theory 675). Calcd for $C_{36}H_{50}O_5Si_4$: C, 64.05; H, 7.46; Si, 16.64. Found: C, 64.09; H, 7.52; Si, 16.43.

17. Bis(dimethylamino)methyl-3,3,3-trifluoropropylsilane

In a two-liter four-necked flask, equipped with a mechanical stirrer, Dry-Ice-acetone condenser, thermometer and addition funnel connected to a nitrogen supply, was placed 500 ml. of petroleum ether, bp 30-60°. After the flask was cooled to -27° with a Dry-Ice-carbon tetrachloride bath, 71 grams (1.58 mole) of anhydrous dimethylamine was added to the petroleum ether in the flask. A solution of 52.7 grams (0.25 mole) of 3,3,3-trifluoropropylmethyldichlorosilane in 70 ml. of petroleum ether (bp 30-60°)

was added to the dimethylamine solution over a period of one hour, a white precipitate formed immediately, and the reaction temperature was kept between -25° and -27° during the addition. The mixture was stirred at -27° for 30 minutes, and then was allowed to warm up to room temperature during the next hour. The excess dimethylamine was passed through a solution of hydrochloric acid during the last 30 minutes of the warming and the amine salt formed was removed by filtration. Fractionation of the filtrate gave 36.5 grams (64%) of bis(dimethylamino)methyl-3,3,3-trifluoropropylsilane: bp 166.5-167°; mass spec (290 eV) m/e 228 and 45; nmr (external TMS) δ -0.217 (s, 3, $SiCH_3$), 0.334-0.835 (m, 2, $SiCH_2$), 1.42-1.92 and 2.22 (m and s, respectively, 14, CCH_2 and NCH_3); F^{19} nmr (external $CFCl_3$) δ -65.7 (t, CF_3). Calcd for $C_8H_{19}F_3N_2Si$: C, 42.06; H, 8.38; F, 24.95; N, 12.26; Si, 12.30. Found: C, 42.16; H, 8.48; F, 24.49; N, 11.55; Si, 12.24.

18. 1,3-Dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-disiloxane (13) and 1,5-Dichloro-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxane (14)

The dichlorodisiloxane 13 and dichlorotrisiloxane 14 were prepared by a modification of the reported method.[4] A mixture of 6.65 grams (0.37 mole) of water and 29.2 grams (0.37 mole) of pyridine was added, under a nitrogen atmosphere, to 158 grams (0.75 mole) of methyl(3,3,3-trifluoropropyl)dichlorosilane in 200 ml. of diethyl ether, over a period of thirty minutes with strong agitation. The resulting mixture was stirred for one additional hour, and then filtered. Fractional distillation of the filtrate gave the following fractions:

Fraction 1: 2.5 grams; bp up to 60°/0.35 Torr; 1.1 mixture of methyl-3,3,3-trifluoropropyldichlorosilane and the dichlorodisiloxane 13.

Fraction 2: 32.7 grams; bp 85-89°/0.1 Torr; crude dichlorodisiloxane 13. (Lit.[4] bp 61-63°/0.6 Torr).

Fraction 3: 4.7 grams; bp 89-110°/0.1 Torr; mixture of dichlorodisiloxane 13 and dichlorotrisiloxane 14.

Fraction 4: 25.7 grams; bp 117-120°/0.1 Torr; crude 1,5-dichlorotrisiloxane 14. Lit.[4] bp 95°/0.6 Torr).

The boiling points observed for the disiloxane and trisiloxane were higher than those reported in the literature. However, these siloxanes, 13 and 14, showed identical retention times to those of authentic samples which were prepared by L. W. Breed.

19. 1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane (16a)

The bis-aminodisiloxane 16a was prepared from 36.7 grams (0.1 mole) of 1,3-dichloro-1,3-dimethyl-1,3-bis(3′,3′,3′-trifluoropropyl)disiloxane and 18 grams (0.4 mole) of anhydrous dimethylamine by the same procedure as described for the preparation of bis(dimethylamino)methyl-3,3,3-trifluoropropylsilane. Distillation of the product gave 26 grams (67.7%) of 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane: bp 237-240°; nmr (external TMS) δ -0.0667 (s, 6, $SiCH_3$), 0.417-0.834 (m, 4, $SiCH_2$), 1.41-2.17 (m, 4, CCH_2) and 2.33 (s, 12, NCH_3); F^{19} nmr (external $CFCl_3$), δ -65.5 (t, CF_3). Calcd for $C_{12}H_{26}F_6N_2OSi_2$: C, 37.49; H, 6.82; N, 7.29. Found: C, 37.34; H, 6.71; N, 6.96.

20. Bis(dimethylamino)dimethylsilane

The reaction of 90 grams (2 moles) of dimethylamine and 64 grams (0.5 mole) of dimethyldichlorosilane, using the same procedure as described for the preparation of bis(dimethylamino)-methyl-3,3,3-trifluoropropylsilane, gave 39 grams (52.7%) of bis(dimethylamino)dimethylsilane: bp 127.5° (Lit.^{5,6} bp   ); nmr (external TMS) δ -0.317 (s, 6, $SiCH_3$) and 2.13 (s, 12, NCH_3).

21. 1,3-Bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane

The reaction of 72 grams (1.6 moles) of dimethylamine and 80.0 grams (0.4 mole) of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, using the same procedure as described for the preparation of bis(dimethylamino)methyl-3,3,3-trifluoropropylsilane, provided 53.8 grams (61.2%) of 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane: bp 173-174.5° (Lit. bp   ); nmr (external TMS) δ -0.15 (s, 12, $SiCH_3$) and 2.27 (s, 12, NCH_3). Calcd for $C_8H_{24}ON_2Si_2$: C, 43.58; H, 10.97; N, 12.71. Found: C, 42.32; H, 11.12; N, 12.42.

22. 1,1,3,3-Tetramethylguanidine Trifluoroacetate

Trifluoroacetic acid (11.4 g., 0.1 mole) and 1,1,3,3-tetramethylguanidine (11.52 g., 0.1 mole) were mixed to form the acid-amine salt.

23. 1,1,3,3-Tetramethylguanidine 2-Ethylhexoate

2-Ethylhexanoic acid (14.4 g., 0.1 mole) and 1,1,3,3-tetramethylguanidine (11.52 g., 0.1 mole) were mixed to form the acid-amine salt.

C. Synthesis of Polymers

1. Polymerization of α,α´-Bis(dimethylhydroxysilyl)-m-xylene

a. With 1,1,3,3-Tetramethylguanidine 2-Ethylhexoate as Catalyst

This polymerization was carried out by a procedure described in the patent literature.[7] In a 100-ml. two-necked flask equipped with a magnetic stirrer, a thermometer, and a water trap connected to a condenser with a calcium sulfate drying tube were placed 10 grams of α,α´-bis(dimethylhydroxysilyl)-m-xylene, 5 ml. of benzene and 0.11 grams of tetramethylguanidine 2-ethylhexoate. The trap was filled with dry benzene and the resulting mixture was heated under a reflux for one hour at 80-90°. Some benzene was removed to raise the temperature of the reaction mixture to 140°. The mixture was kept at that temperature for four hours and then heated at 160° and 0.2 Torr for 21 hours. The gummy product formed was dissolved in 35 ml. of toluene, and the polymer was precipitated with 30 ml. of methanol. The precipitate was washed twice with 30-ml. portions of methanol and dried at 200° and 0.2 mm. for 4 hours to yield 6.7 grams of poly(1,1,3,3-tetramethyldisiloxanylene-m-xylylene): nmr ($CDCl_3$) δ 0.017 (s, 12, $SiCH_3$), 2.0 (s, 4, $SiCH_2$) and 6.6-7.4 (m, 4, ArH); number average molecular weight [determined by high-speed membrane osmometry (MO] 41,750. Calcd for $C_{12}H_{20}O_1Si_2$: C, 60.95; H, 8.53; Si, 23.75. Found: C, 60.96; H, 8.72; Si, 23.72. Sublimation of white solids were noticed at the top of the reaction flask after six hours of heating. The solids were collected and recrystallized from 95% ethanol to yield 0.5 grams of 2,4,13,15-tetrasila-3,14-dioxa-2,2,4,4,13,13,15,15-octamethyl [5.5] metacyclophane: white needles; mp 114°.

b. With 1,1,3,3-Tetramethylguanidine Trifluoroacetate as Catalyst

The same procedure as described in C.1.a was used except for the following changes:

1. Tetramethylguanidine trifluoroacetate was used as the catalyst.

2. The reaction was carried out for 64 hours at 160° 0.1 Torr.
3. The product was dried for 20 hours at 190° and 0.1 Torr.

This polymerization provided 8.6 grams of poly(1,1,3,3-tetramethyldisiloxanylene-m-xylylene): viscous gum; intrinsic viscosity (toluene at 30°) 0.362 dl/g; molecular weight (benzene, VPO) 10,300. Calcd for $C_{12}H_{20}OSi_2$: C, 60.95; H, 8.53; Si, 23.75. Found: C, 60.95; H, 8.75; Si, 23.80.

2. Poly[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-disiloxanylene-m-xylylene]

a. With 1,1,3,3-Tetramethylguanidine 2-Ethylhexoate as Catalyst

This polymerization was carried out by a procedure described in patent literature[7]. In a 100-ml. two-necked flask equipped with a magnetic stirrer, a thermometer, and a water trap connected to a condenser with a calcium sulfate drying tube were placed 10 grams of 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl-m-xylylene]-1,3-bis(3,3,3-trifluoropropyl)disiloxane, 5 ml. of benzene and 0.11 gram of tetramethylguanidine 2-ethylhexoate. The trap was filled with dry benzene and the resulting mixture was heated under a reflux for one hour at 80-90°. Some benzene was removed to raise the temperature of the reaction mixture to 140°. The mixture was kept at that temperature for four hours and then heated at 160° and 0.2 Torr for 21 hours. The gummy product formed was dissolved in 35 ml. of toluene, and the polymer was precipitated with 30 ml. of methanol. The precipitate was washed twice with 30-ml. portions of methanol then dried at 190° and 0.2 mm. for 16 hours to yield 6.7 grams of poly[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-disiloxanylene-m-xylylene]: translucent light brown gum; intrinsic viscosity (toluene at 30°) 0.142 dl/g; number average molecular weight (benzene, ML) 41,300; nmr (C_6D_6, external TMS) δ -0.0334, 0.0167, 0.217 (four s, 6, $SiCH_3$), 0.5-1.0 (m, 4, $SiCH_2$), 1.42-2.25 (m, 8, CCH_2 and $SiCH_2Ar$) and 6.58-7.35 (m, 4, ArH). Calcd for $C_{16}H_{22}F_6OSi_2$: C, 47.98; H, 5.54; F, 28.46; Si, 14.03. Found: C, 47.44; H, 5.67; F, 27.21; Si, 13.28.

b. With Ferric Chloride as Catalyst

A mixture of 9.08 grams (0.02 mole) of α,α´-bis[chloromethyl-(3,3,3-trifluoropropyl)-m-xylene and 0.92 gram (0.02 mole) of absolute ethanol was heated at 70° for two hours under nitrogen and then cooled. Ferric chloride (0.135 g., 1.5 weight %) was added to the flask, and the resulting mixture was heated at 120° for 16 hours. The mixture was dissolved in toluene (50 ml.), washed with water several times, dried over anhydrous magnesium sulfate and filtered. The solvent was removed by evaporation on a rotary evaporator to yield crude polymer. The polymer was dissolved in 10 ml. of toluene and precipitated with 50 ml. of methanol to give 0.7 gram of poly[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxanylene-m-xylylene] after drying for 24 hours at 120°: molecular weight (benzene, VPO), 7400. Calcd for $C_{16}H_{22}F_6OSi_2$: C, 47.98; H, 5.54. Found: C, 46.71; H, 5.65.

c. By Copolymerization

A mixture of 1.13 grams (2.5 mmoles) of α,α´-bis[chloromethyl(3,3,3-trifluoropropyl)]-m-xylene and 1.11 grams (2.5 mmoles) of α,α´-bis[methoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene, together with 16.5 mg. (0.1 mmole) of anhydrous ferric chloride, was heated at 200° for 8 hours under reduced pressure[8] which was gradually decreased to 6 Torr. The color of the reaction mixture changed from red to gray while only a small change in viscosity was noted. Additional ferric chloride (~16 mg.) was added to the mixture which was heated again for 6 hours at 200° and 3 Torr. The polymer formed was dissolved in 30 ml. of toluene, precipitated with 30 ml. of methanol, separated, washed twice with methanol, and dried at 170° for 16 hours at 0.1 Torr. The polymer weighed one gram and was an extremely viscous, drak brown gum: intrinsic viscosity (in toluene at 30°) 0.1921 dl/g. Calcd for $C_{16}H_{22}F_6OSi_2$: C, 47.98; H, 5.57. Found: C, 47.16; H, 5.78.

A small amount of white solid which sublimed onto the thermometer and walls of the reaction flask were dissolved in acetone. Evaporation of the acetone gave white needles: mp 101-109°.

Recrystallization of the solids from n-hexane gave 1.5 milligrams of a cyclic dimer: mp 105-107°; mass spec (290 eV), m/e 656, 641, 403 and 328; ir 10.55 cm^{-1} for SiOSi. Calcd for $C_{36}H_{48}O_4Si_4$: C, 65.80; H, 7.36. Found: C, 64.65; H, 7.29.

3. Poly(1,1,3,3-tetramethyldisiloxanylenemethylene-3,3´-oxydiphenylenemethylene)

a. With 1,1,3,3-Tetramethylguanidine 2-Ethylhexoate as Catalyst

This polymerization was carried out by a procedure described in the patent literature.[7] In a 100-ml. two-necked flask equipped with a magnetic stirrer, a thermometer, and a water trap connected to a condenser with a calcium sulfate drying tube were placed 10 grams of 1,3-bis[dimethylhydroxysilylmethylene-3,3´-oxydiphenylenemethylene]-1,1,3,3-tetramethyldisiloxane, 5 ml. of benzene and 0.11 gram of tetramethylguanidine 2-ethylhexoate. The trap was filled with dry benzene and the resulting mixture was heated under a reflux for one hour at 80-90°. Some benzene was removed to raise the temperature of the reaction mixture to 140°. The mixture was kept at that temperature for four hours and then heated at 160° and 0.2 Torr for 21 hours. The gummy product formed was dissolved in 30 ml. of toluene, and the polymer was precipitated with 30 ml. of methanol. The precipitate was washed twice with 30-ml. portions of methanol, then dried at 200° and 0.1 mm. for 16 hours to yield 9.5 grams of poly(1,1,3,3-tetramethyldisiloxanylenemethylene-3,3´-oxydiphenylenemethylene): nmr (CCl_4) δ 0.005 (broad, 12, $SiCH_3$), 2.0 (broad, 4, $SiCH_2$), 6.49-7.26 (m, 8, ArH); number average molecular weight (benzene, VPO), 7200; intrinsic viscosity (toluene at 30°) 0.131. Calcd for $C_{18}H_{24}O_2Si_2$: C, 65.80; H, 7.36; Si, 17.10. Found: C, 65.93; H, 7.42; Si, 17.16.

4. Poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]

In a 100-ml. three-necked flask, equipped with a thermometer, stirrer, nitrogen inlet, and condenser which was connected to a solution of hydrochloric acid, were placed α,α´-bis(dimethylhydroxysilyl)-m-xylene (12.7 g., 0.05 mole), 10.5 grams of bis(dimethylamino)-

3,3,3-trifluoropropylmethylsilane and 20 ml. of toluene. The mixture was warmed to 110° and, when the temperature reached 85°, dimethylamine began to evolve. After heating the mixture for 15 minutes, an additional 0.9 gram of bis(dimethylamino)-3,3,3-trifluoropropylmethylsilane, was added dropwise over 5 minutes. The mixture was heated for 1.5 hours (or for a total of two hours), and then hydrolyzed with 1.5 ml. of water. Water was removed as an azeotrope after which the polymer formed was dissolved in 50 ml. of toluene, filtered, and precipitated with 50 ml. of methanol. The precipitate was washed twice with 30 ml. of methanol, and dried at 170° and 0.1 Torr for two hours to yield 15.4 grams of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene]: translucent viscous sticky gum; number average molecular weight (benzene, MO), 33,000; intrinsic viscosity (toluene at 30°), 0.243 dl/g; nmr (CCl_4, external TMS) δ -0.1 and 0.0333 (two s, 15, $SiCH_3$), 0.25-0.75 (m, 2, $SiCH_2$), 1.5-2.0 and 2.0 (m and s, 6, CCH_2 and $SiCH_2Ar$) and 6.5-7.15 (m, 4, ArH); F^{19} nmr ($CFCl_3$), δ -64.3 (t, CF_3). Calcd for $C_{16}H_{27}F_3O_2Si_3$: C, 48.95; H, 6.93. Found: C, 49.31; H, 7.81.

5. Poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)-trisiloxanylene-*m*-xylylene

Poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)-trisiloxanylene-*m*-xylylene] was prepared by the same procedure as described for the preparation of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene], from 6.3 grams (0.015 mole) of α,α'-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl-m-xylene and 2.22 grams (0.015 mole) of bis(dimethylamino)dimethylsilane. After work-up and drying of the product at 190° and 0.1 Torr for 16 hours, 4.7 grams of the desired polymer was obtained: nmr (CCl_4, external TMS) δ -0.0166 and 0.0833 (two s, 12, $SiCH_3$), 0.5-1.0 (m, 4, $SiCH_2$), 1.33-2.5 (m, 8, CCH_2 and $SiCH_2Ar$) and 6.5-7.24 (m, 4, ArH); F^{19} nmr (Ext. $CFCl_3$) δ -64.3 (t, CF_3); number average molecular weight (benzene, VPO), 21,000. Calcd for $C_{18}H_{28}F_6O_2Si_3$; C, 45.55; H, 5.95. Found: C, 45.91; H, 5.98.

The toluene and methanol washings were combined and evaporated on a rotary evaporator to leave 1.8 grams of low molecular weight polymer: number average molecular weight (benzene, VPO) 4200. Calcd for $C_{18}H_{28}F_6O_2Si_3$: C, 45.55; H, 5.95. Found: C, 45.86; H, 6.19.

6. Poly[1,3,3-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene]

Poly[1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene] was prepared from 6.3 grams (0.015 mole) of α,α′-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl-*m*-xylene and 3.43 grams (0.015 mole) of bis(dimethylamino)methyl(3,3,3-trifluoropropyl)silane, using the same procedure as described for the preparation of poly[1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene]. The product was dried at 190° and 0.1 Torr for 16 hours to yield 7.5 grams of polymer: nmr (CCl_4, external TMS) δ -0.0334 and 0.1 (two s, 8.1, $SiCH_3$), 0.334-1.0 (m, 6.18, $SiCH_2$), 1.335-2.5 (m, 10.5, CCH_2 and $SiCH_2Ar$) and 6.5-7.26 (m, 4, ArH); F^{19} nmr ($CFCl_3$), δ -64.6 (t, CF_3); number average molecular weight (tetrahydrofuran, VPO) 17,000. Calcd for $C_{20}H_{29}F_9O_2Si_3$: C, 43.15; H, 5.25. Found: C, 43.15; H, 5.48.

7. Poly[1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene] with Pendant Vinyl Groups

Poly[1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene with 3 mole percent of vinylmethylsiloxy groups was prepared from 6.3 grams (0.015 mole) of α,α′-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl-*m*-xylene and a mixture of 3.32 grams (14.55 mmoles) of bis(dimethylamino)methyl(3,3,3-trifluoropropyl)silane and 71.28 milligrams (0.45 mmole) of bis(dimethylamino)methylvinylsilane, using the same procedure as described for the preparation of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene]. After work-up, the product was dried at 200° and 0.1 Torr for 16 hours to yield 6.2 grams of polymer: readily soluble in tetrahydrofuran: number average molecular weight (tetrahydrofuran, VPO) 21,000; inherent viscosity (0.5% solution in tetrahydrofuran at 30°) 0.16 dl/g.

8. Poly[1,1,3,3,5,5-hexamethyltrisiloxanylene-*m*-xylylene] (*19a*)

Polymer *19a* was prepared from 12.5 grams (0.05 mole) of α,α′-bis(dimethylhydroxysilyl)-*m*-xylene and 7.4 grams (0.05 mole) of bis(dimethylamino)dimethylsilane, by the same procedure as described for the preparation of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene]. Evaporation of the solvent on a rotary evaporator following work-up gave 14 grams of a liquid residue which solidified on standing overnight at room temperature. Drying of the solid at 200° and 1 Torr for 16 hours provided a white waxy solid polymer: mp 63.5-64.5°; nmr (CCl_4, external TMS) δ -0.0667 and 0.0166 (two s, 18, $SiCH_3$), 2.0 (s, 4, $SiCH_2$) and 6.5-7.0 (m, 4, ArH); number average molecular weight (benzene, VPO) 14,500; intrinsic viscosity (toluene at 30°) 0.355 dl/g. Calcd for $C_{14}H_{26}O_2Si_3$: C, 54.14; H, 8.44; Si, 27.13. Found: C, 54.37; H, 8.80; Si, 27.06.

9. Poly[1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3,3,3-trifluoropropyl)tetrasiloxanylene-*m*-xylylene] (*20c*)

The polymer *20c* was prepared from 6.27 grams (0.015 mole) of α,α′-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]-*m*-xylene and 4.92 grams (0.015 mole) of 1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-1,3-bis(dimethylamino)disiloxane, by the same procedure as described for the preparation of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-*m*-xylylene]. The polymer formed was insoluble in 30 ml. of toluene, but the addition of a small amount of methanol provided a clear solution. The product was precipitated by adding more methanol, separated, washed three times with 30 ml. of methanol, and dried at 200° and 1 Torr for 16 hours to yield 7.3 grams of polymer *20c*: clear and transparent gum; readily soluble in tetrahydrofuran; number average molecular weight (tetrahydrofuran, VPO) 22,000; inherent viscosity (0.5% solution in tetrahydrofuran at 30°) 0.142 dl/g. Calcd for $C_{24}H_{36}F_{12}O_3Si_4$: C, 40.44; H, 5.09. Found: C, 40.66; H, 5.21.

10. Poly[1,1,3,5,7,7-hexamethyl-3,5-bis(3,3,3-trifluoropropyl)-tetrasiloxanylene-*m*-xylylene] (*20b*)

Polymer *20b* was prepared from 4.45 grams (17.5 mmoles) of α,α′-bis(dimethylhydroxysilyl)-*m*-xylene and 6.6 grams (17.5 mmoles) of 1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-1,3-bis(dimethylamino)disiloxane, using the same procedure as described for the preparation of poly[1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)-trisiloxanylene-m-xylylene]. The crude product was dissolved in hot toluene (30 ml.), filtered, precipitated with 25 ml. of methanol, washed twice with 30-ml. portions of methanol, and dried for 16 hours at 260° and 0.1 Torr to yield 5 grams of polymer 20b: very viscous fluid; number average molecular weight (tetrahydrofuran, VPO) 13,000; inherent viscosity (0.5% solution in tetrahydrofuran at 30°) 0.08 dl/g; nmr (CCl_4, external TMS) -0.02 and 0.02 (two s, 18, $SiCH_3$, two types at 2:1 ratio) 0.8-0.3 (m, 4, $SiCH_2$) 2.0 and 2.1-1.4 (s and m, 8, $SiCH_2Ar$ and CCH_2CF_3) and 7.1-6.5 (m, 4, ArH). Calcd for $C_{20}H_{34}F_6O_3Si_4$: C, 43.77; H, 6.24. Found: C, 44.29; H, 6.62.

The toluene and methanol solution was evaporated on a rotary evaporator to leave a viscous fluid. The fluid was dried for 16 hours at 260° and 0.1 Torr to yield one gram of polymer 20b with molecular weight of 9,000 (tetrahydrofuran, VPO). In another experiment using 0.05 mole of each monomer, 20 grams of polymer 20b was obtained. The polymer showed the following properties: inherent viscosity (0.5% solution in tetrahydrofuran at 30°) 0.37 dl/g; number average molecular weight (tetrahydrofuran, VPO) 17,000. Calcd for $C_{20}H_{34}F_6O_3Si_4$: C, 43.77; H, 6.24. Found: C, 44.32; H, 6.58.

11. Poly[1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-m-xylylene] (20a)

a. By Solution Polymerization

Polymer 20a was prepared from 7.62 grams (0.03 mole) of α,α′-bis(dimethylhydroxysilyl)-m-xylene and 6.60 grams (0.03 mole) of 1,1,3,3-tetramethyl-1,3-bis(dimethylamino)disiloxane, using the same procedure as described for the preparation of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]. The product was dried at 200° and 0.1 Torr for 16 hours to yield 8.8 grams of polymer 20a: nmr (CCl_4, external TMS) δ -0.0167 (s, 12, $SiCH_3$), 0.0334 (s, 12, $SiCH_3$), 2.0 (s, 4, $SiCH_2$), and 6.5-7.0 (m, 4, ArH); number average molecular weight (benzene, VPO) 14,000; inherent viscosity (0.5% solution in tetrahydrofuran at 30°) 0.35 dl/g. Calcd for $C_{16}H_{32}O_3Si_4$: C, 49.94; H, 8.38; Si, 29.20. Found: C, 49.32; H, 8.66; Si, 28.67.

b. By Bulk Polymerization

Polymer *20a* was also prepared by a bulk polymerization. A mixture of 7.62 grams (0.03 mole) of α,α′-bis(dimethylhydroxysilyl)-*m*-xylene and 4.83 grams (0.015 mole) of decamethyl-1,5-diazo-3,7-dioxa-2,4,6,8-tetrasilaoctane[9] was heated under nitrogen at 160° for 8 hours. The reaction mixture was dissolved in 15 ml. of toluene, and then hydrolyzed with 1 ml. of water. Water and toluene were removed azeotropically. The resulting mixture was dissolved in 30 ml. of toluene, precipitated with 25 ml. of methanol, washed twice with 25-ml. portions of methanol and dried for 18 hours at 200° and 1 Torr to yield 10 grams of polymer *20a*: inherent viscosity (0.5% solution in toluene at 30°) 0.35 dl/g; number average molecular weight (benzene, VPO) 17,000. Calcd for $C_{16}H_{32}O_3Si_4$: C, 49.95; H, 8.38; Si, 29.20. Found: C, 49.66; H, 8.74; Si, 29.07.

Polymer *20a* was also prepared by a second bulk polymerization reaction. The polymerization was carried out as described above, using a mixture of 7.62 grams (0.03 mole) of α,α′-bis(dimethyldydroxysilyl)-*m*-xylene and 6.60 grams (0.03 mole) of 1,1,3,3-tetramethyl-1,3-bis(dimethylamino)disiloxane. The yield of polymer *20a* was 10.4 grams with a number average molecular weight of 8010 as determined by vapor phase osmometry in benzene.

D. General Procedures for Vulcanization

1. Method A

A mixture of 100 parts of polymer and 2 parts of the peroxide Vulcup R (trade mark of Hercules, Inc.) was thoroughly mixed, placed in a Teflon mold (with inside dimension of 1/2" x 1 1/2" x 0.020" and outside dimensions of 1.25" x 2.25" x 0.5") without a cover, and cured for one hour at 190°. Under these conditions, the surface of the polymer remained uncured, probably due to the inhibition of free radical reaction in the presence of oxygen. The uncured surface was washed and removed with n-hexane to obtain the cured test specimen.

2. Method B

The polymers were mixed with two weight-percent (based on the polymer) of Vulcup R, and the resulting mixtures were compression molded for 30 minutes at 170° and 2000 psi. using a stainless steel mold (with inside dimensions of 1" x 3" x 0.040" and outside dimensions of 1.75" x 3.75" x 0.375") and a Teflon cover (1.75" x 3.75" x 0.25"). Vulcanizates of 1" x 3" x 0.040" sheet were obtained from 2.5 gram samples of the polymers. The vulcanizates were post-cured for 16 hours at 120° and 0.1 Torr.

Molded sheets with dimensions of 0.5" x 1.5" x 0.020" were obtained similarly by using a smaller mold and 0.5 gram samples of the polymers.

E. Determination of Volume Swell Ratios of Elastomers

The elastomeric vulcanizates were immersed for 72 hours at room temperature in JP-4 jet fuel and/or iso-octane. The thickness of the vulcanizates was measured before and after immersion to determine the change in length. The volume swell ratio of the vulcanizate was calculated according to ASTM Method D 1460-60.[10]

SECTION IV

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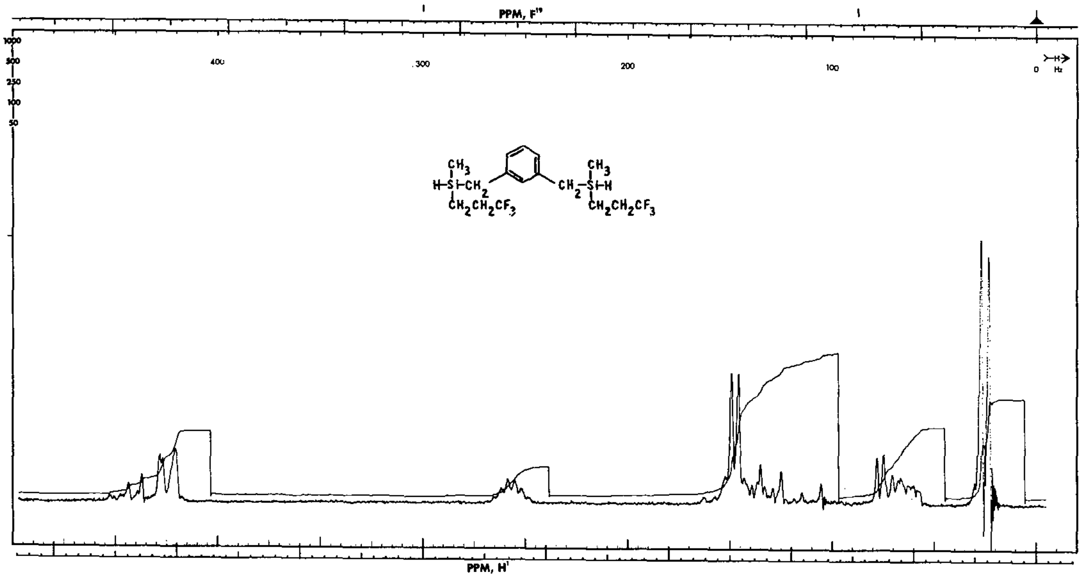

Figure 14. NMR spectrum of α,α'-bis[3,3,3-trifluoropropylmethylsilyl]-m-xylene

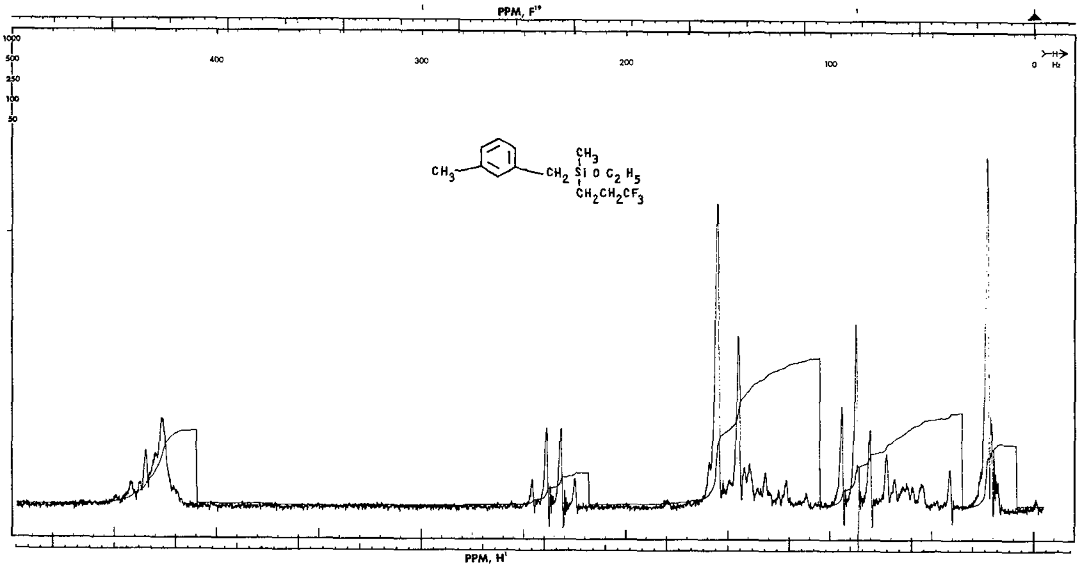

Figure 15. NMR spectrum of α-[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

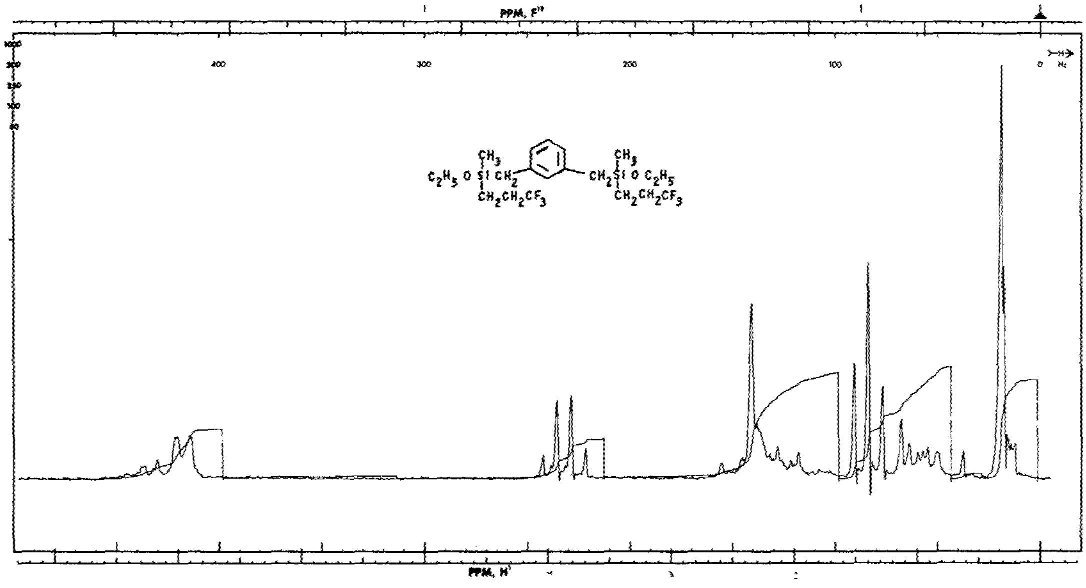

Figure 16. NMR spectrum of α,α´-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

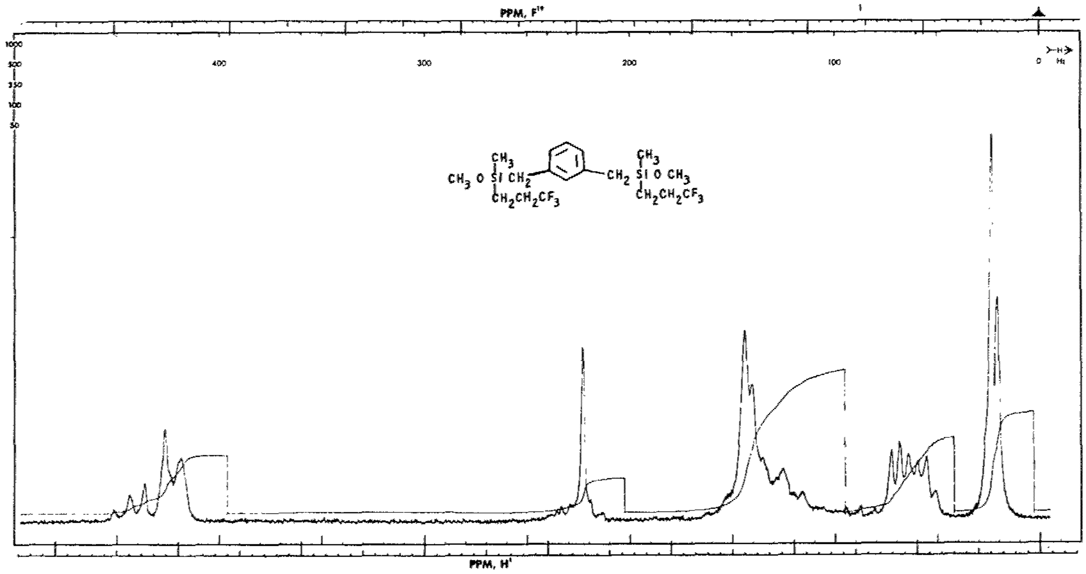

Figure 17. NMR spectrum of α,α´-bis[methoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

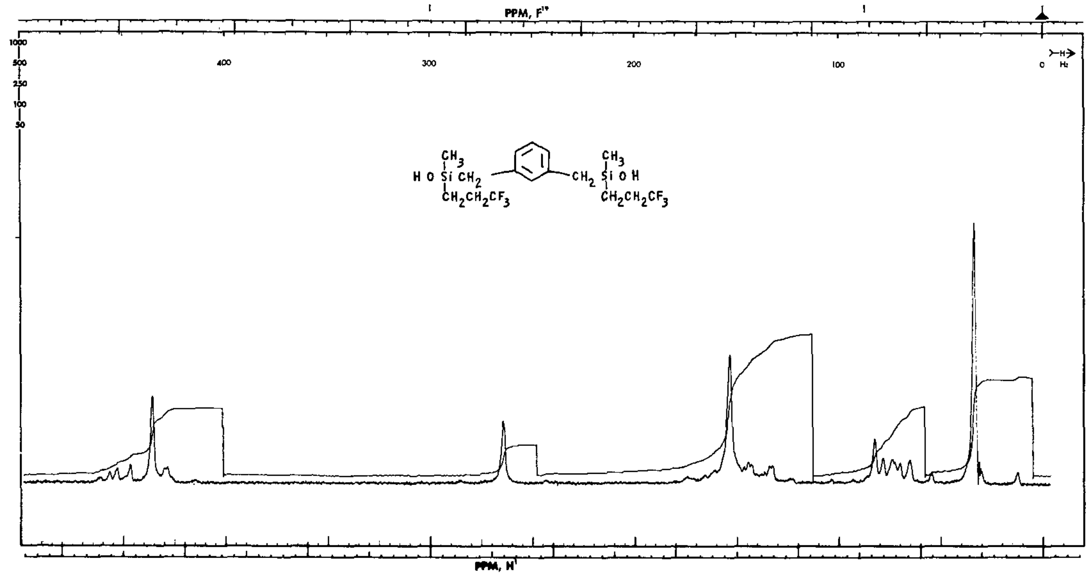

Figure 18. NMR spectrum of α,α′-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

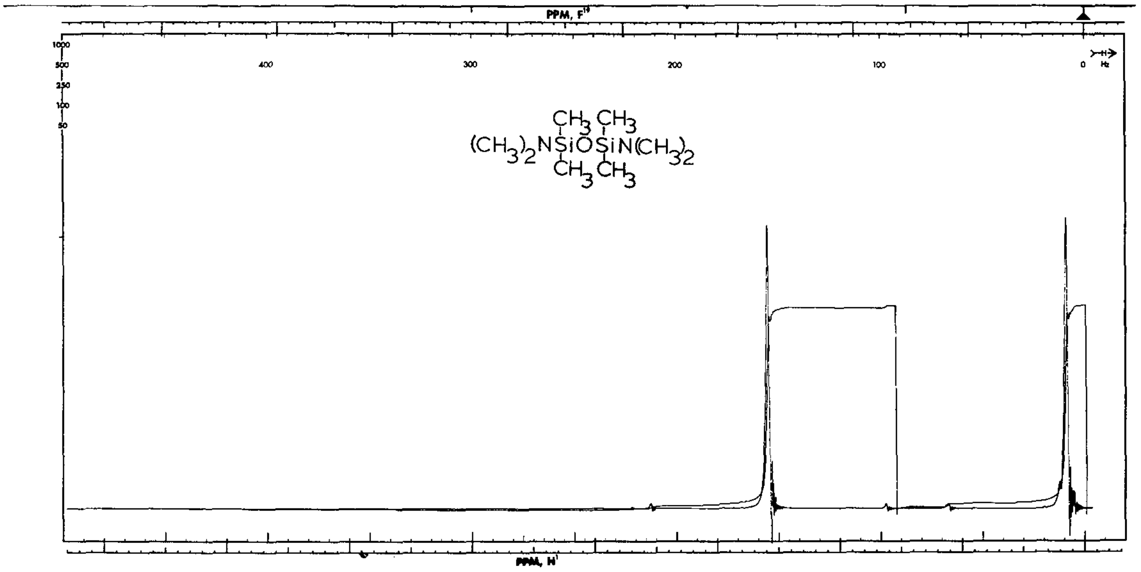

Figure 19. NMR spectrum of 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane

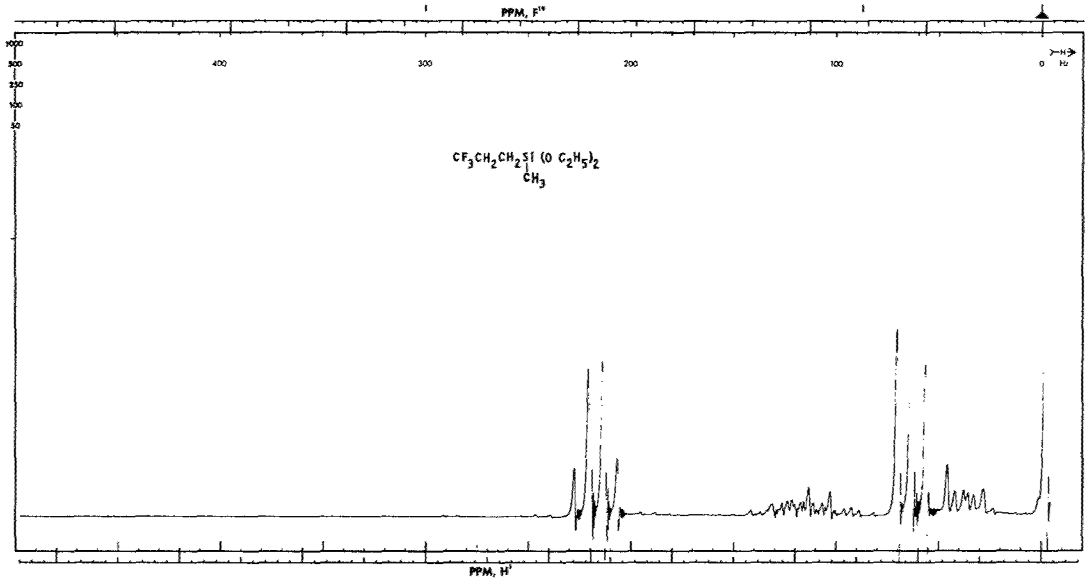

Figure 20. NMR spectrum of 3,3,3-trifluoropropyldiethoxymethylsilane

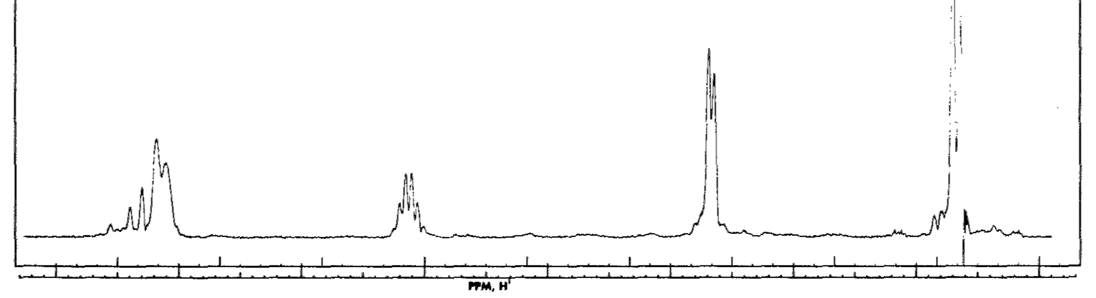

Figure 21. NMR spectrum of α,α′-bis[chloromethylsilyl]-*m*-xylene

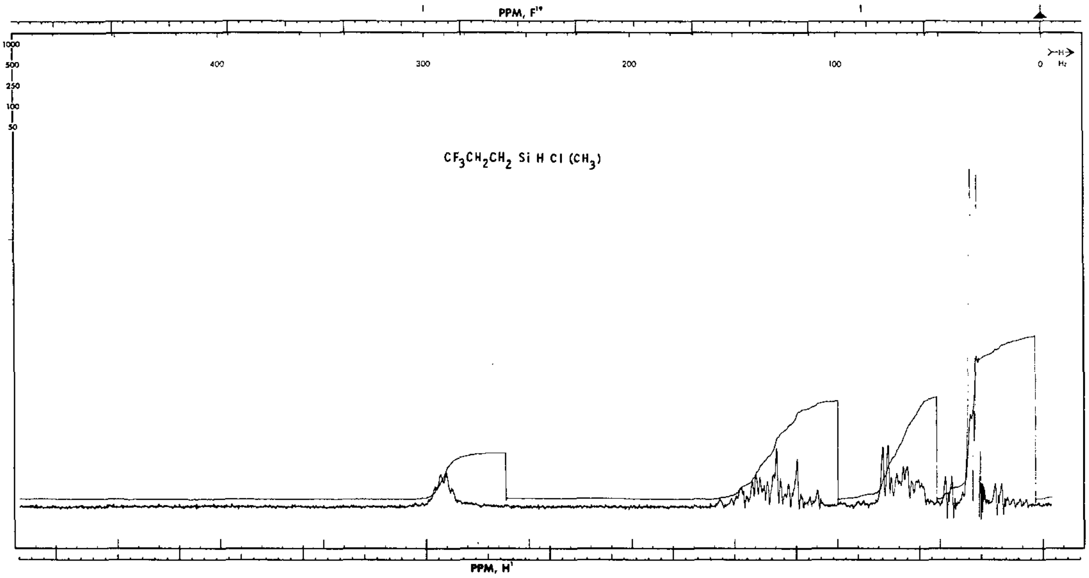

Figure 22. NMR spectrum of methyl(3,3,3-trifluoropropyl)-chlorosilane

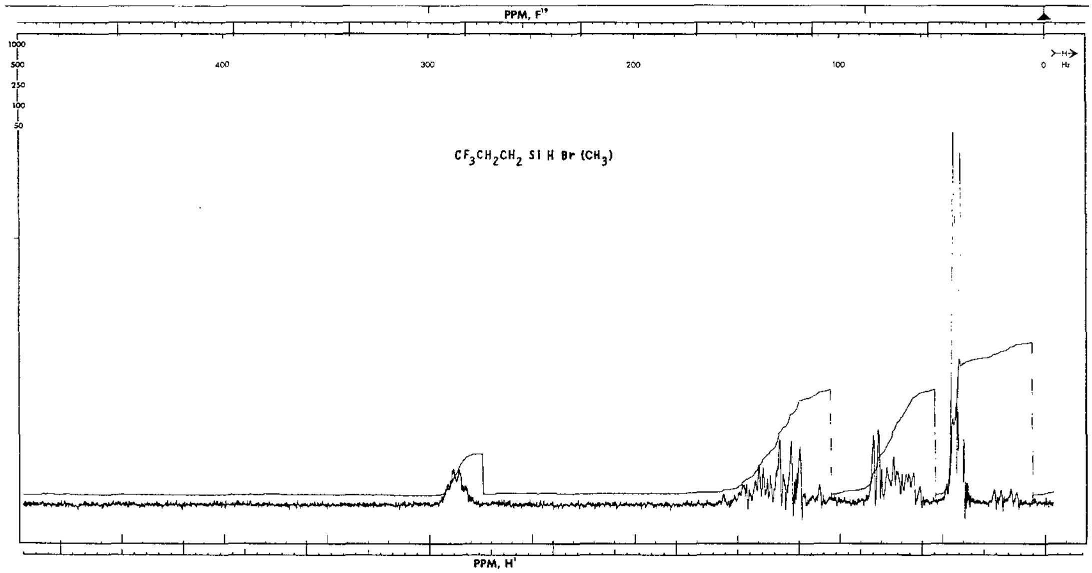

Figure 23. NMR spectrum of methyl(3,3,3-trifluoropropyl)-bromosilane

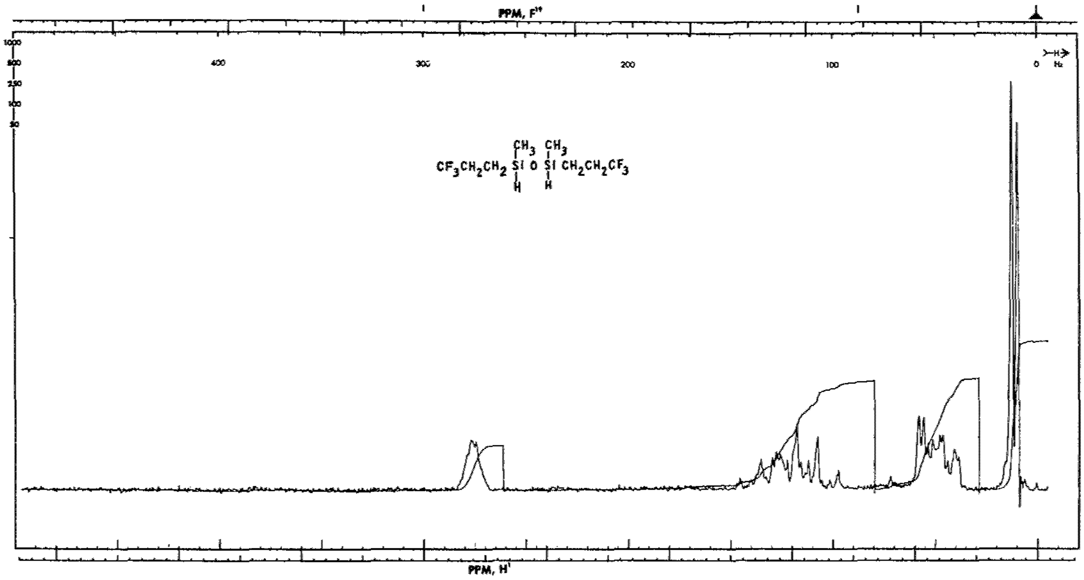

Figure 24. NMR spectrum of 1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

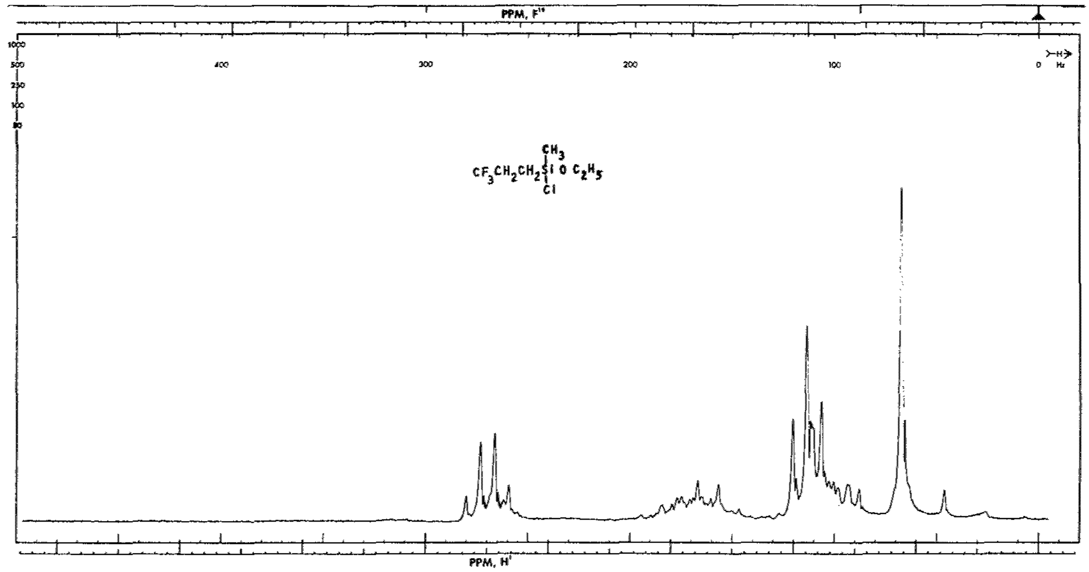

Figure 25. NMR spectrum of chloroethoxymethyl(3,3,3-trifluoropropyl)silane

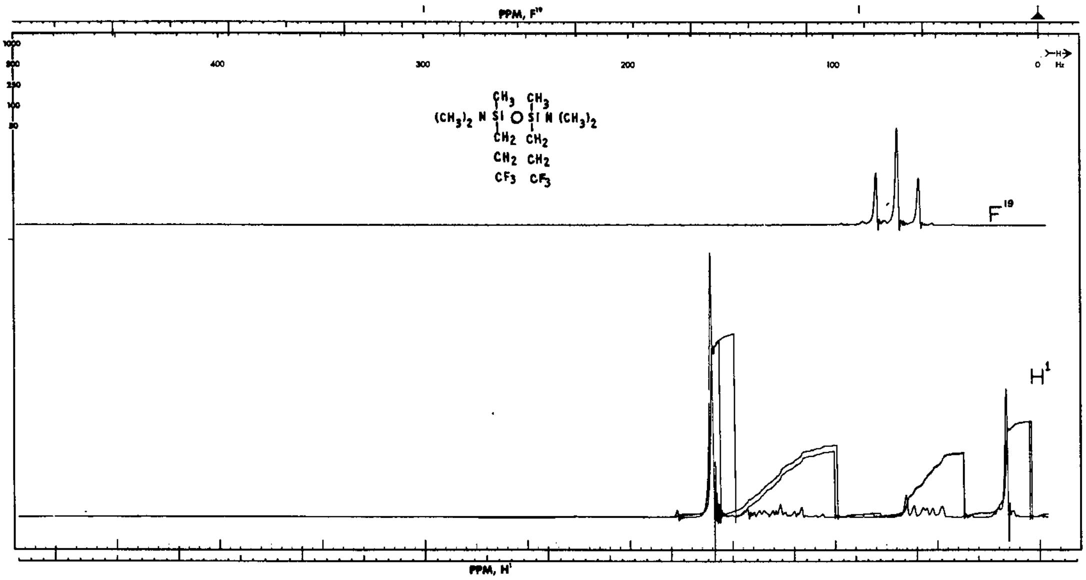

Figure 26. NMR spectrum of 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

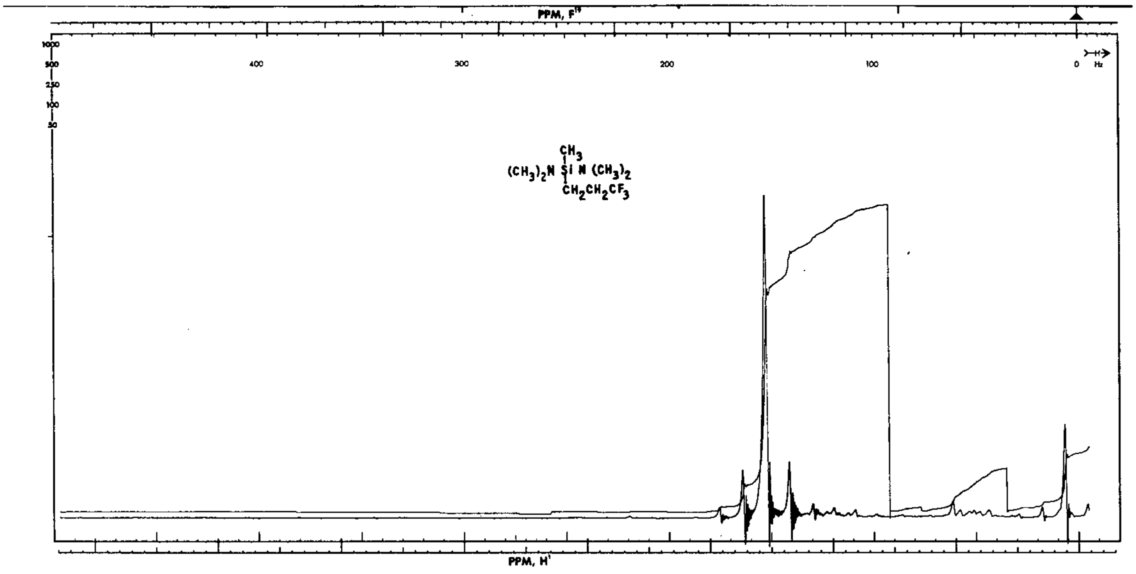

Figure 27. NMR spectrum of bis(dimethylamino)methyl(3,3,3-trifluoropropyl)silane

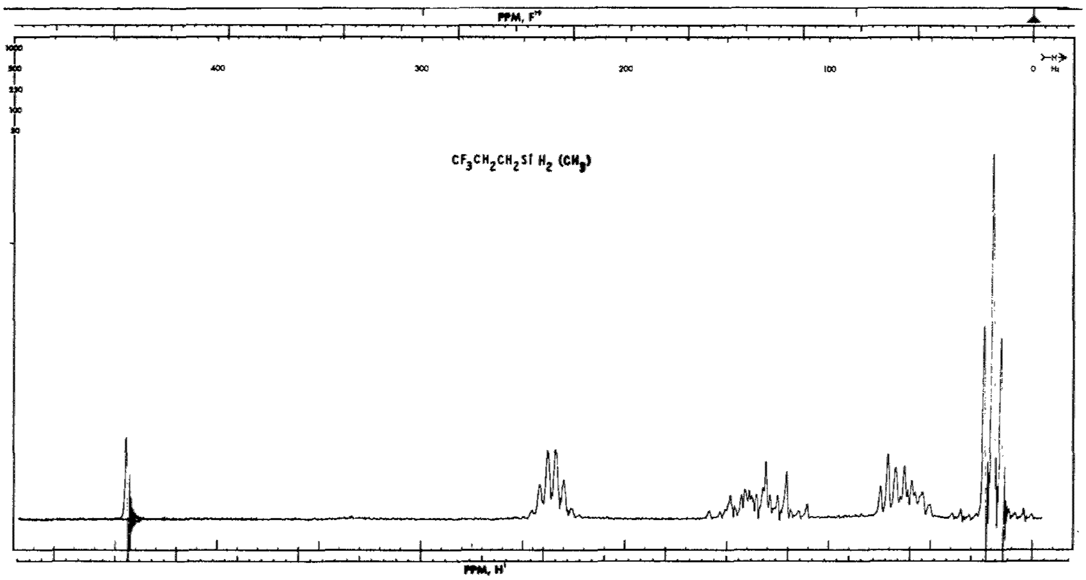

Figure 28. NMR spectrum of methyl(3,3,3-trifluoropropyl)-silane

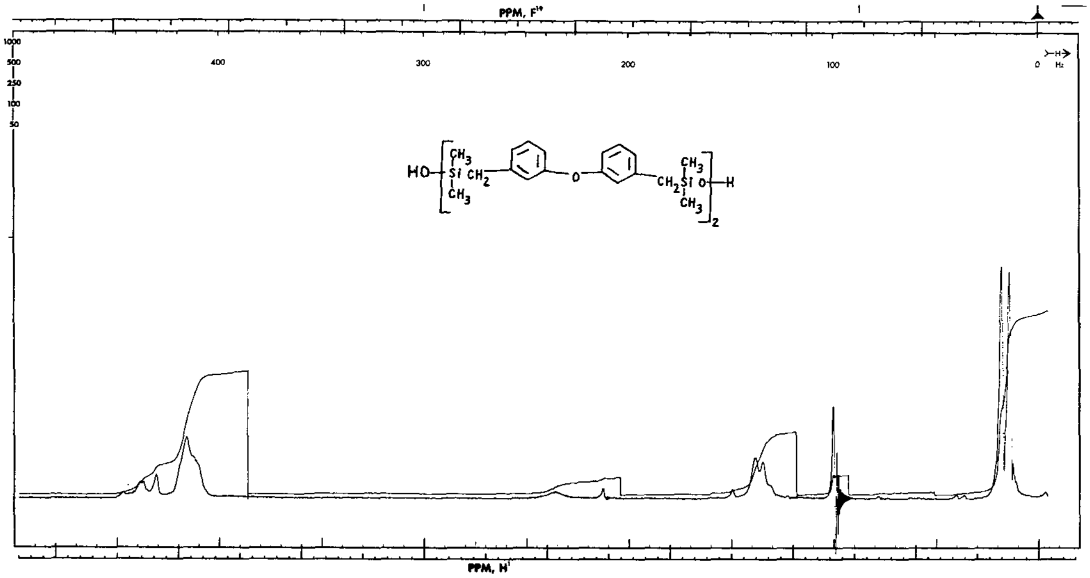

Figure 29. NMR spectrum of 1,3-bis(dimethylhydroxysilylmethylene-3,3´-oxydiphenylenemethylene)-1,1,3,3-tetramethyldisiloxane

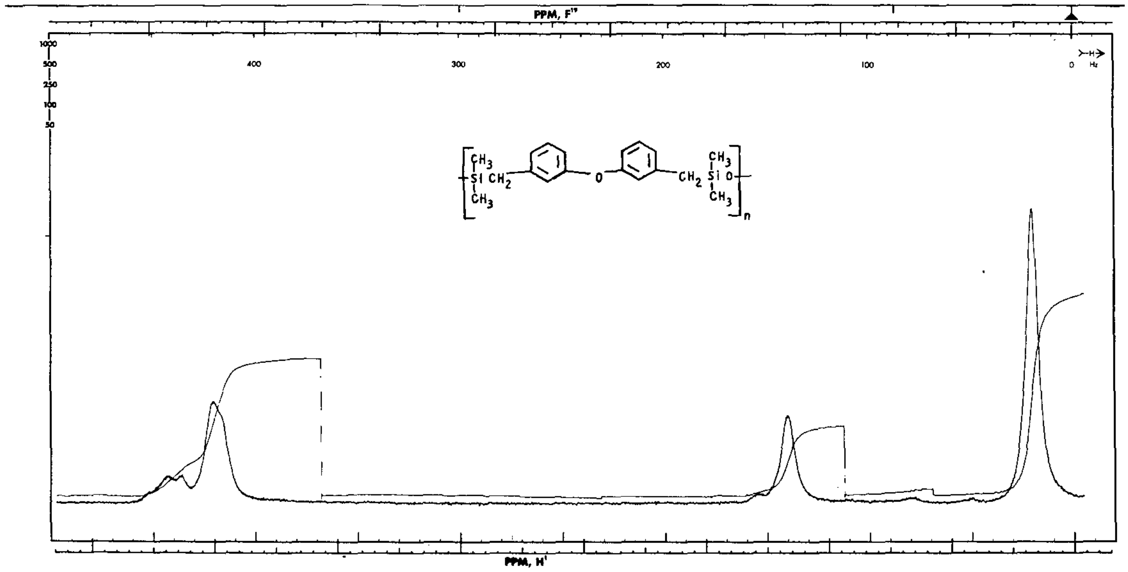

Figure 30. NMR spectrum of poly(1,1,3,3-tetramethyldisiloxanylenemethylene-3,3´-oxydiphenylenemethylene

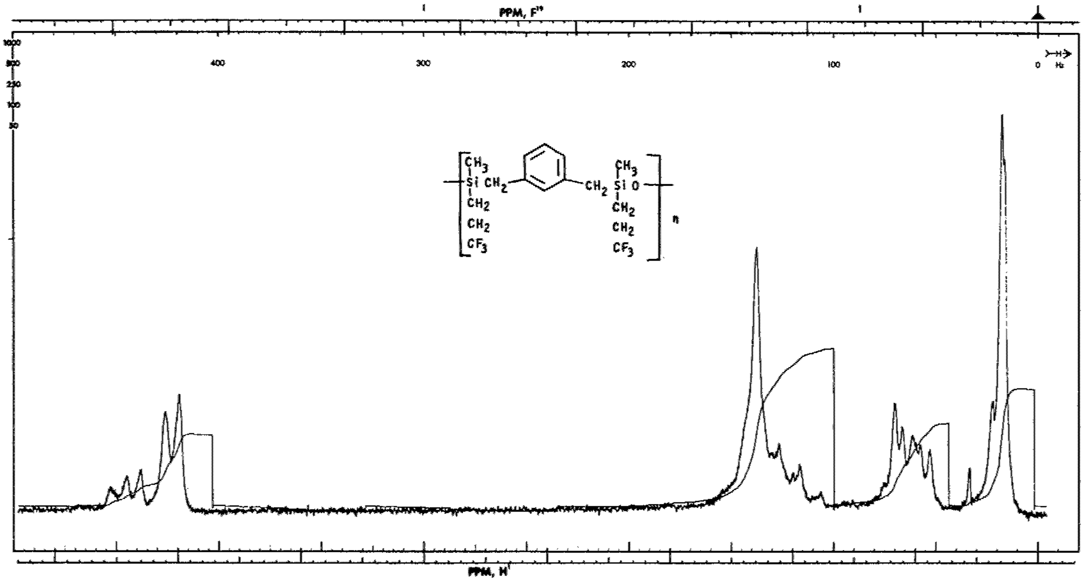

Figure 31. NMR spectrum of poly[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxanylene-m-xylylene]

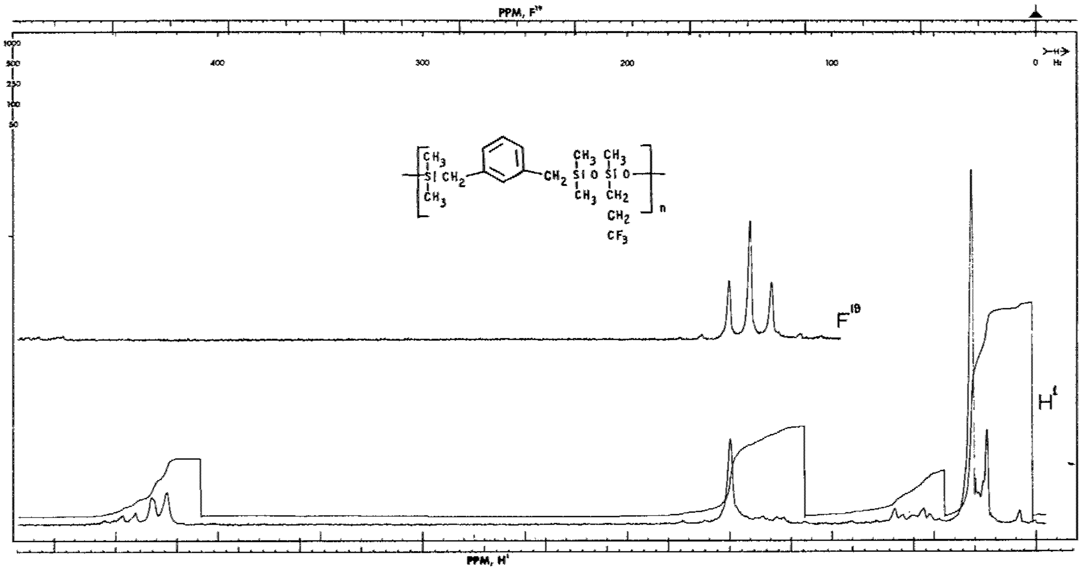

Figure 32. NMR spectrum of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]

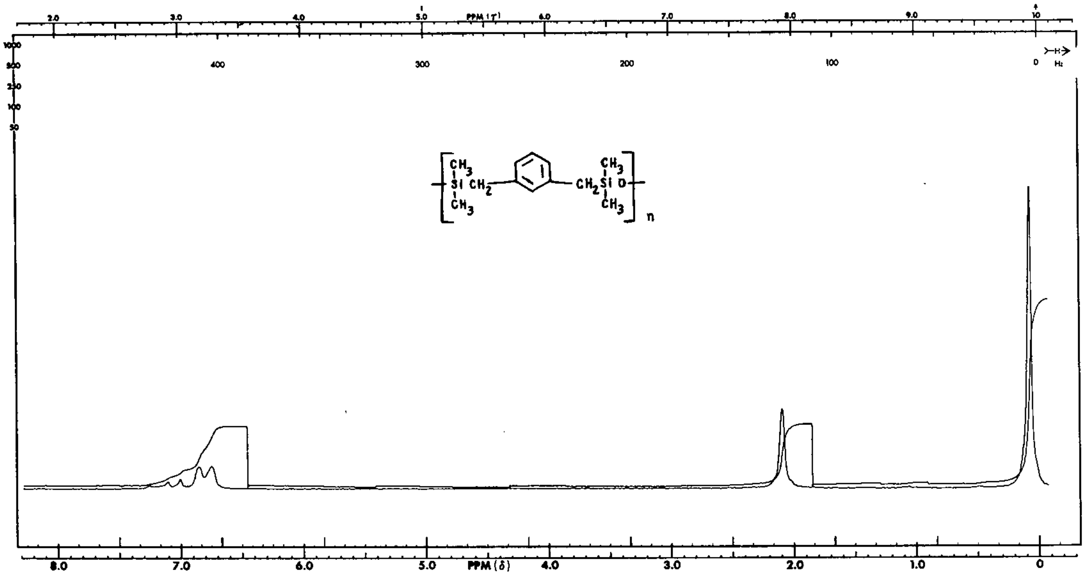

Figure 33. NMR spectrum of poly(1,1,3,3-tetramethyldisiloxanylene-m-xylylene)

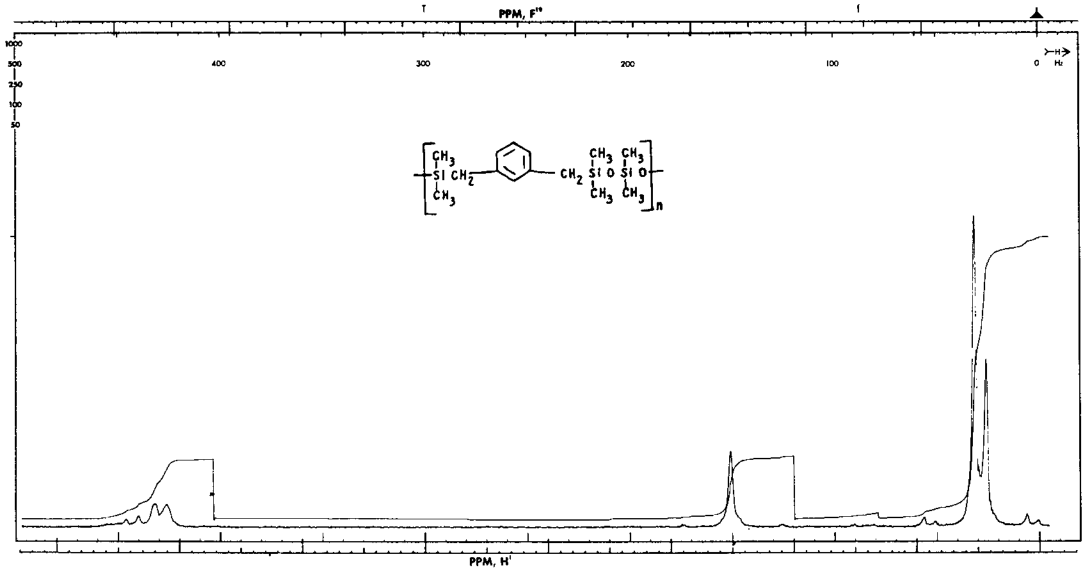

Figure 34. NMR spectrum of poly(1,1,3,3,5,5-hexamethyltrisiloxanylene-m-xylylene)

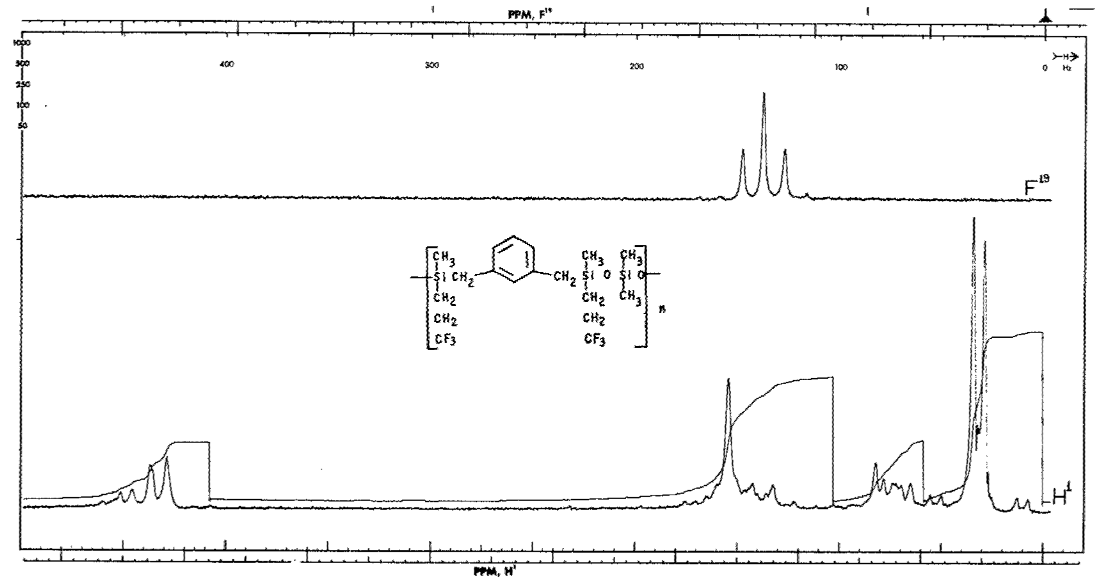

Figure 35. NMR spectrum of poly[1,3,3,5-tetramethyl-1,5-bis-(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]

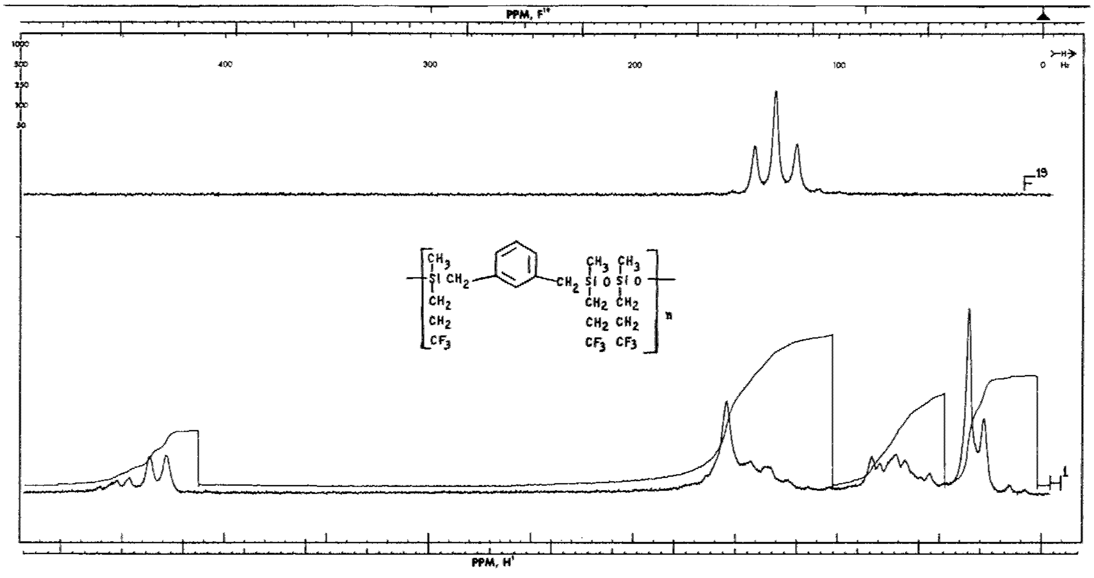

Figure 36. NMR spectrum of poly[1,3,5-trimethyl-1,3,5-tris-(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene

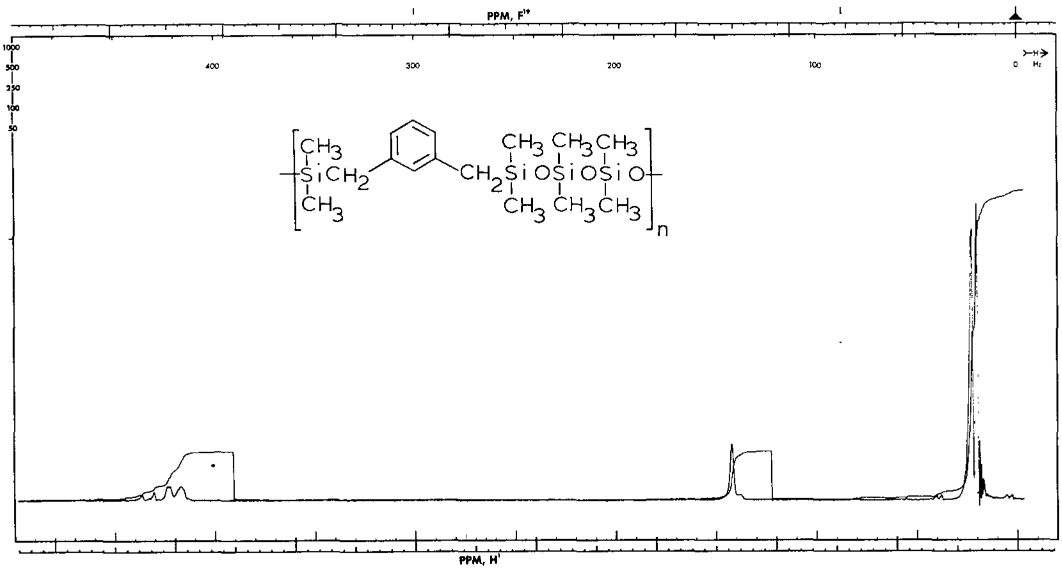

Figure 37. NMR spectrum of poly[1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-m-xylylene]

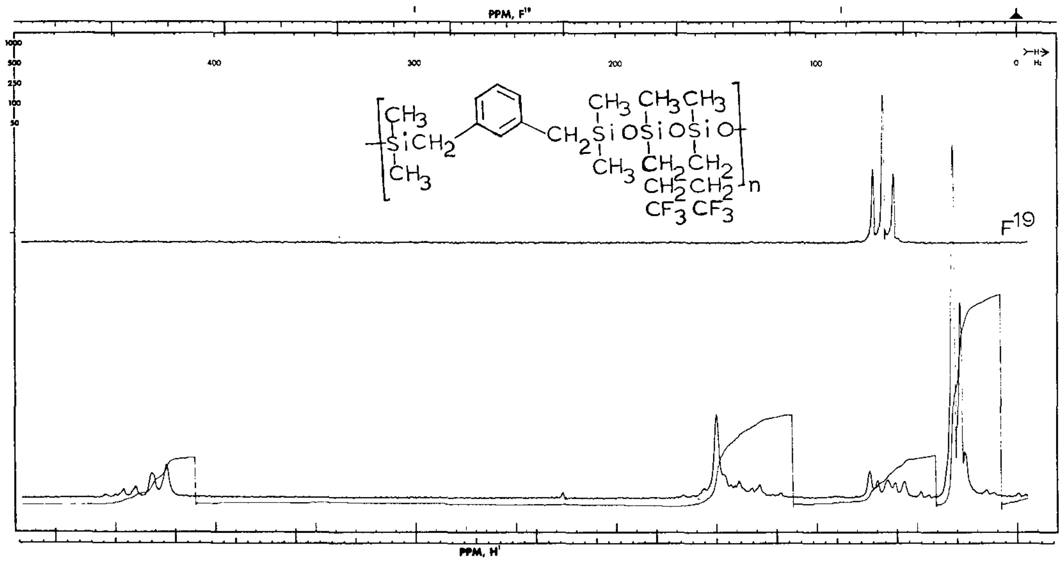

Figure 38. NMR spectrum of poly[1,1,3,5,7,7-hexamethyl-3,5-bis(3,3,3-trifluoropropyl)tetrasiloxanylene-m-xylylene]

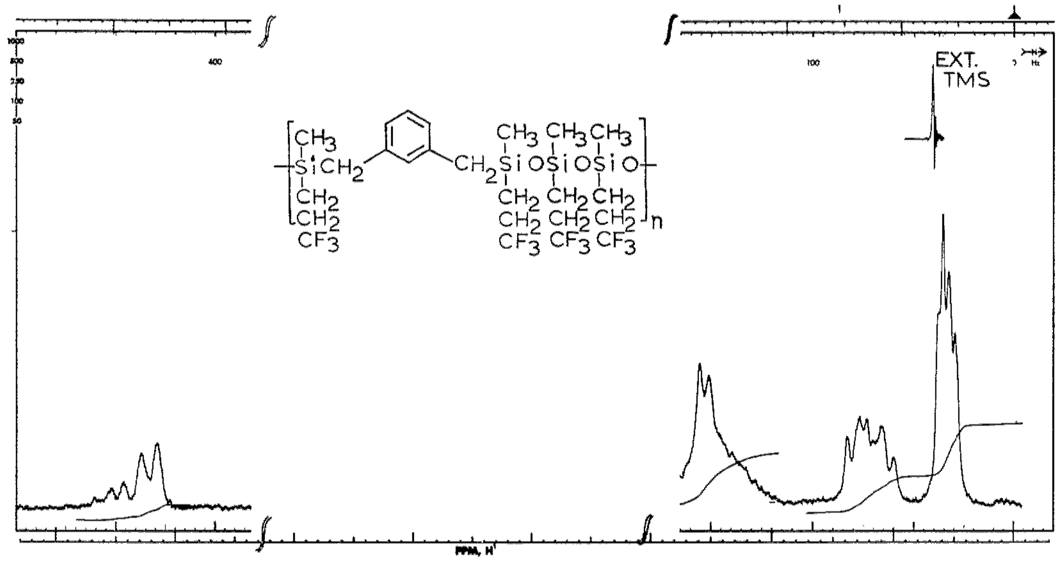

Figure 39. NMR spectrum of poly[1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3,3,3-trifluoropropyl)tetrasiloxanylene-m-xylylene]

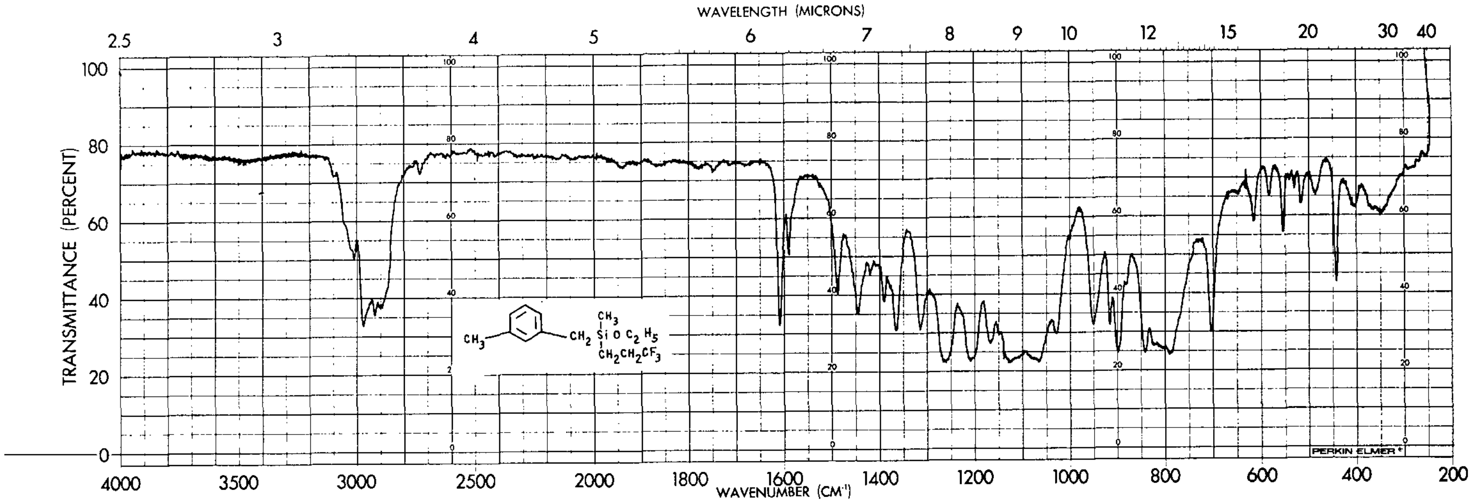

Figure 40. Infrared spectrum of α-[ethoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

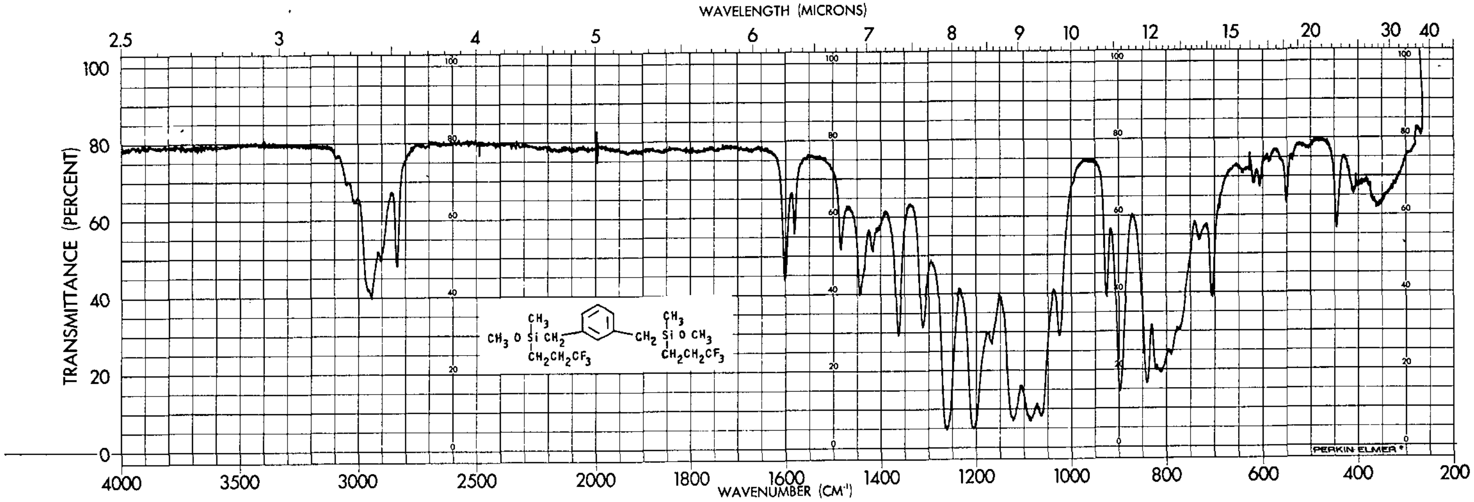

Figure 41. Infrared spectrum of α,α′-bis[methoxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

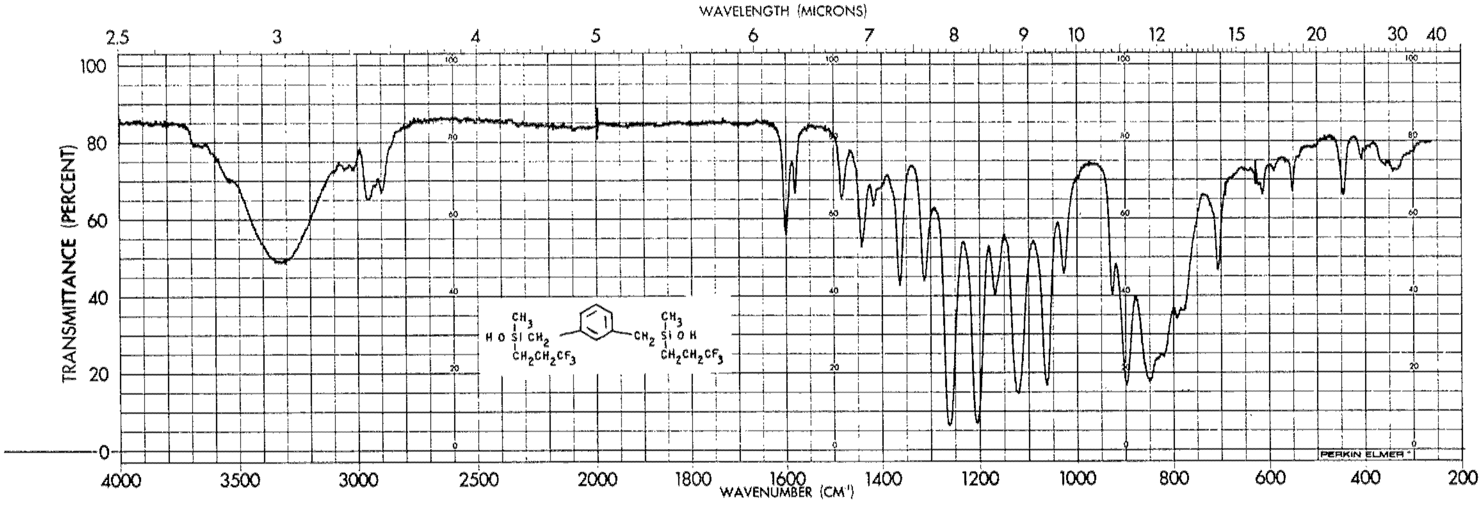

Figure 42. Infrared spectrum of α,α′-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]-m-xylene

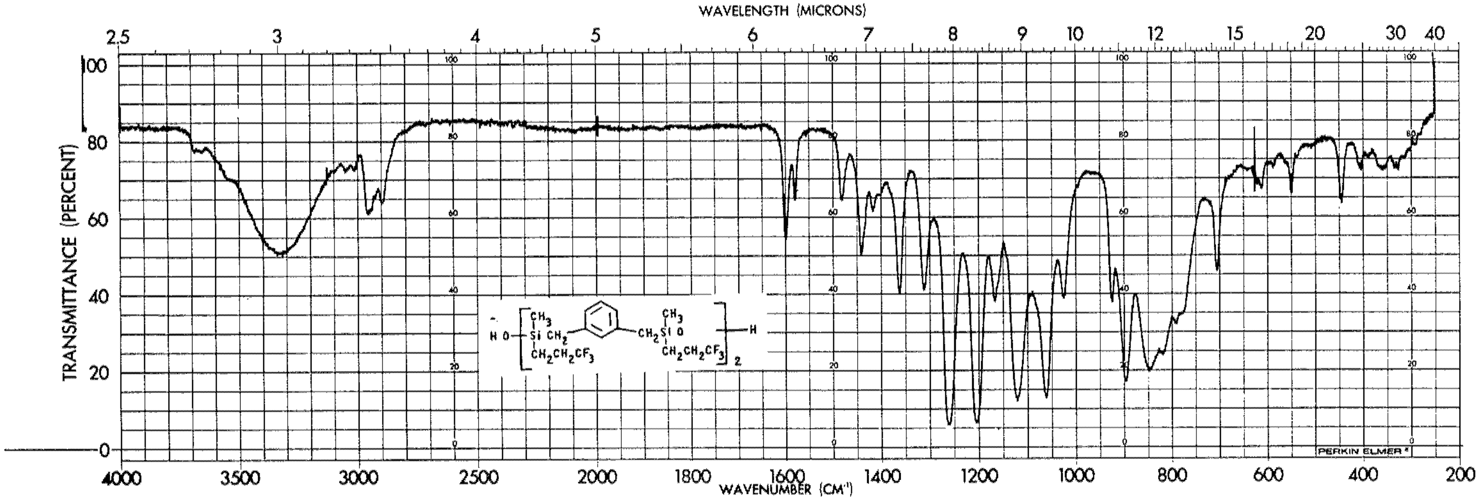

Figure 43. Infrared spectrum of 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl-m-xylylene]-1,3-dimethyl-1,3-bis-(3,3,3-trifluoropropyl)disiloxane

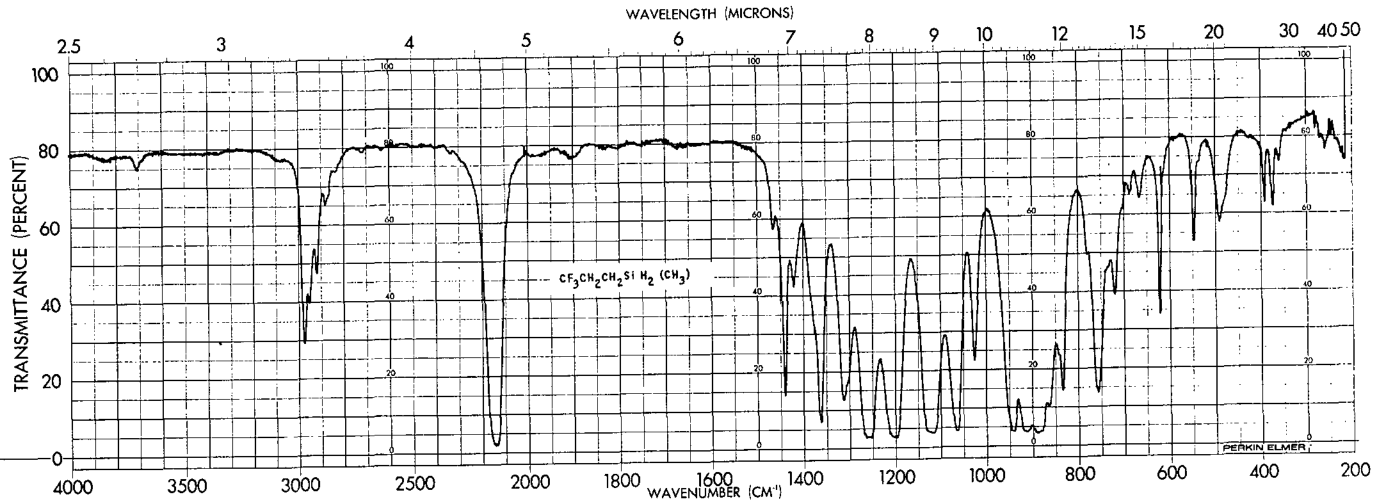

Figure 44. Infrared spectrum of 3,3,3-trifluoropropylmethylsilane

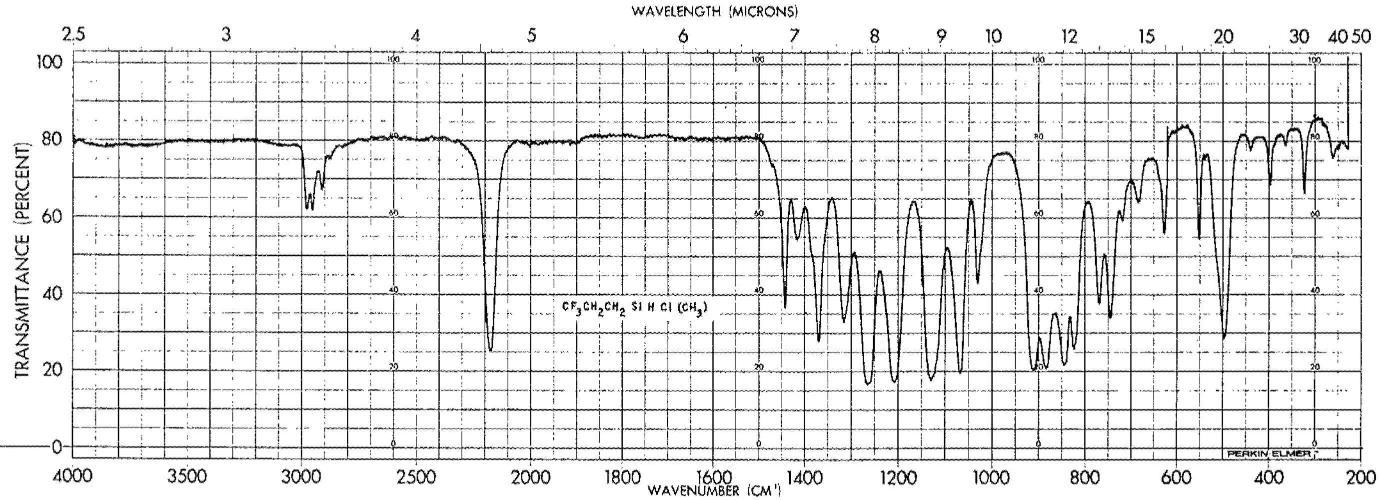

Figure 45. Infrared spectrum of methyl(3,3,3-trifluoropropyl)-chlorosilane

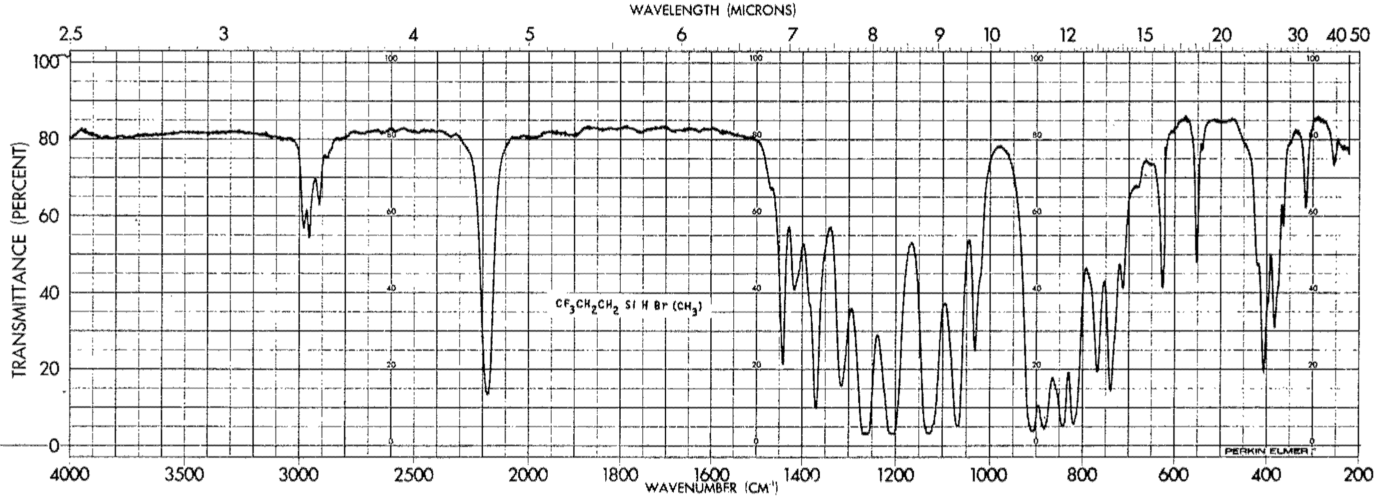

Figure 46. Infrared spectrum of methyl(3,3,3-trifluoropropyl)-bromosilane

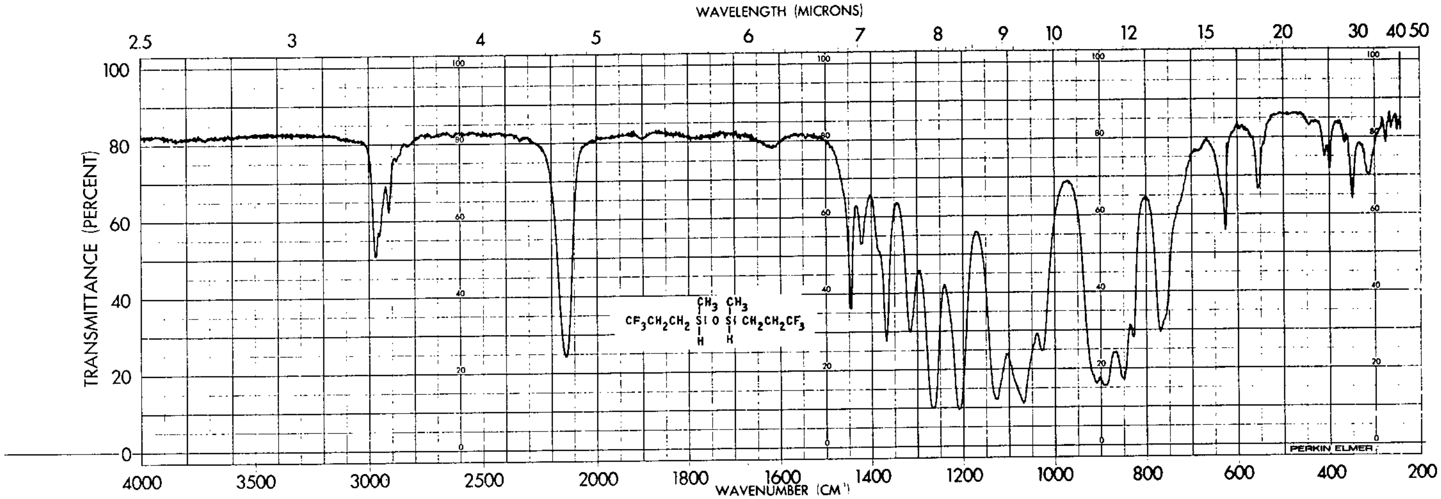

Figure 47. Infrared spectrum of 1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

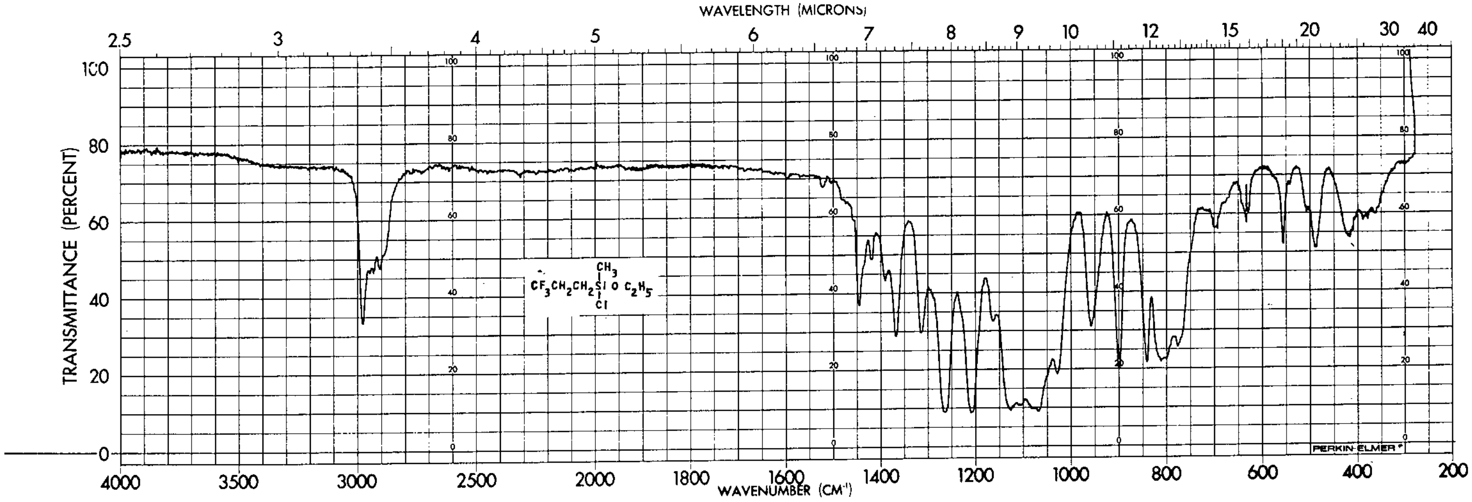

Figure 48. Infrared spectrum of chloroethoxymethyl(3,3,3-trifluoropropyl)silane

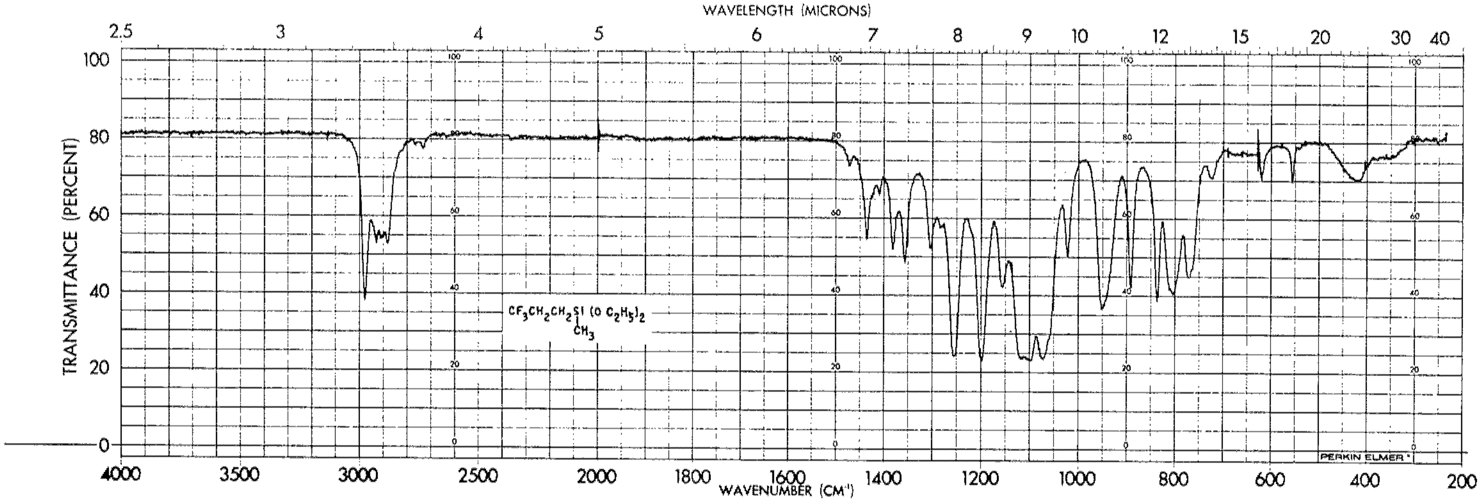

Figure 49. Infrared spectrum of diethoxymethyl(3,3,3-trifluoropropyl)silane

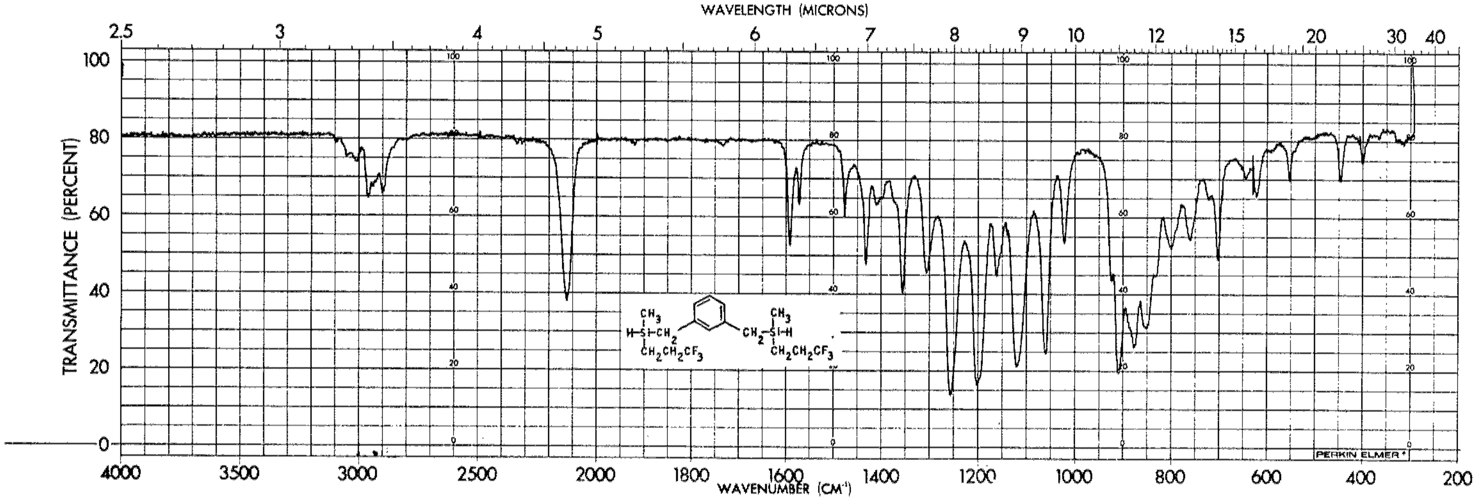

Figure 50. Infrared spectrum of α,α´-bis(3,3,3-trifluoropropylmethylsilyl)-m-xylene

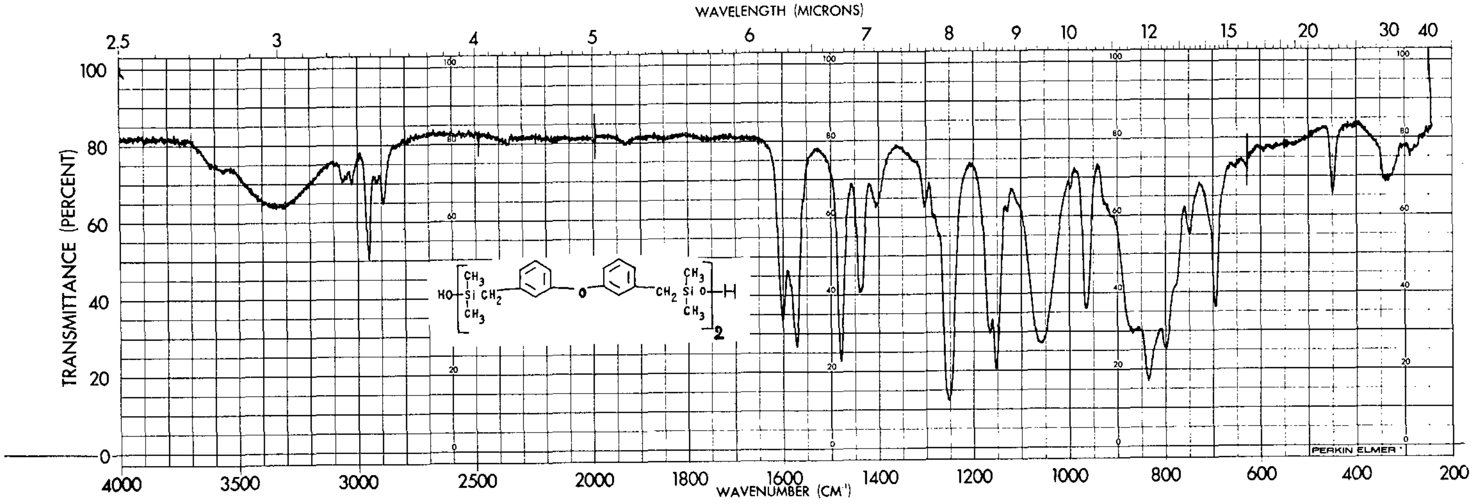

Figure 51. Infrared spectrum of 1,3-bis(dimethylhydroxysilylmethylene-3,3′-oxydiphenylenemethylene)-1,1,3,3-tetramethyldisiloxane

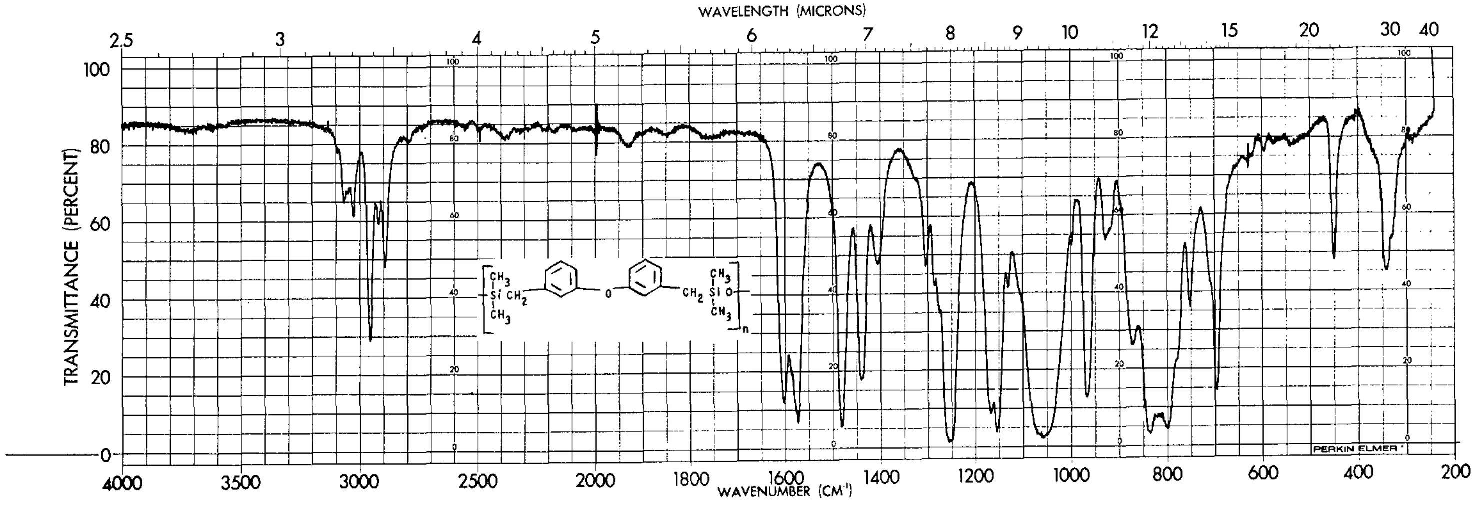

Figure 52. Infrared spectrum of poly(1,1,3,3-tetramethyldisiloxanylene-3,3′-oxydiphenylenemethylene)

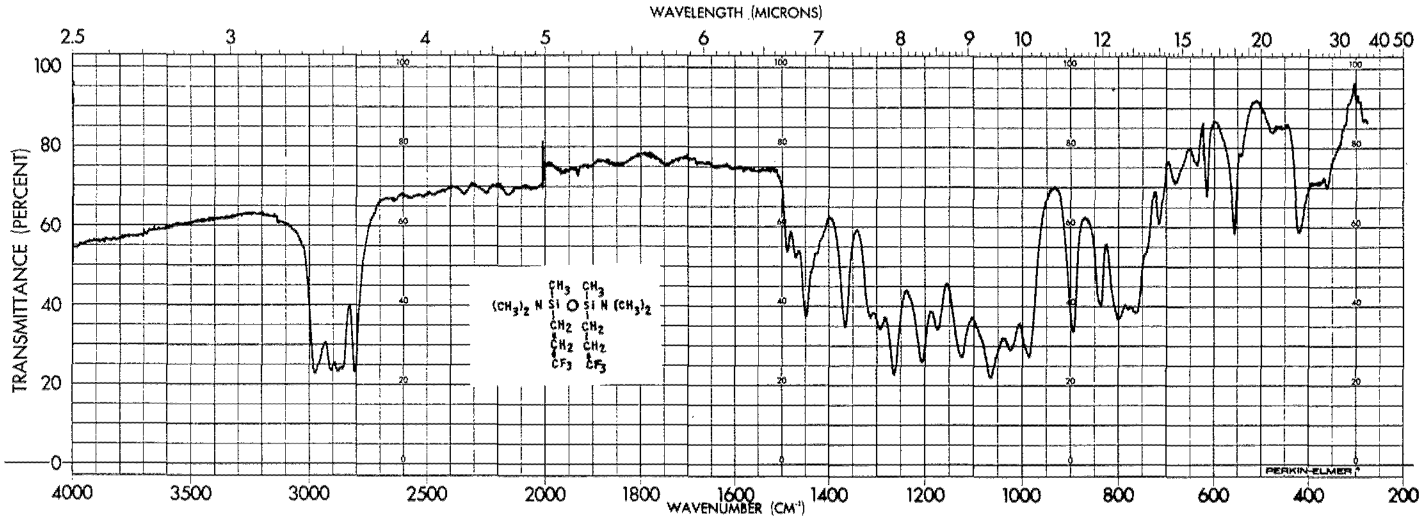

Figure 53. Infrared spectrum of 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

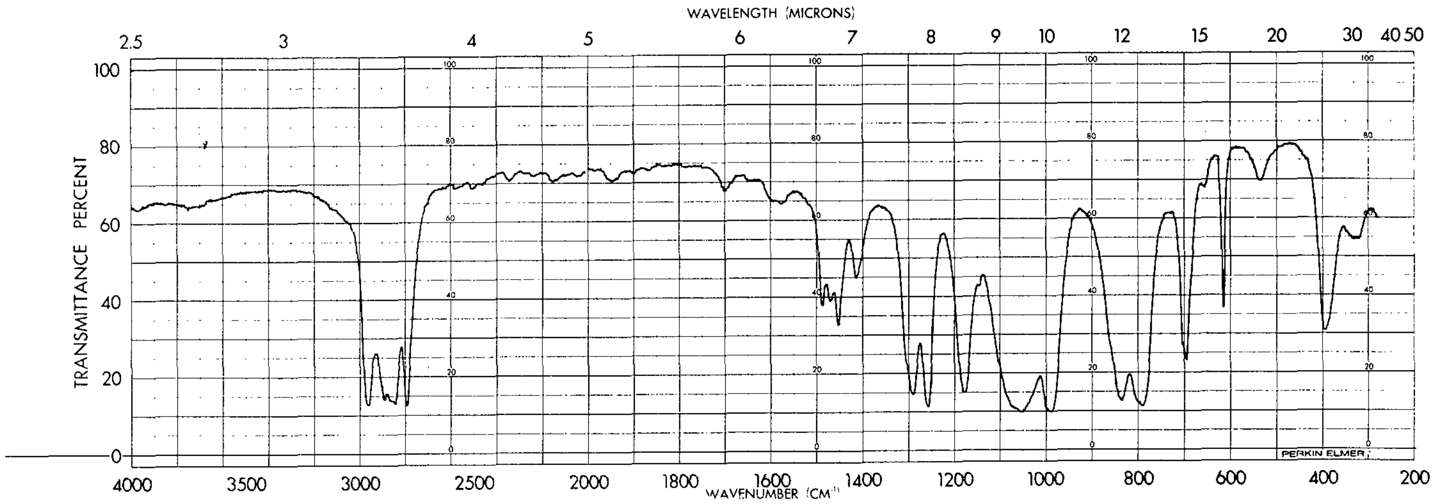

Figure 54. Infrared spectrum of 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane

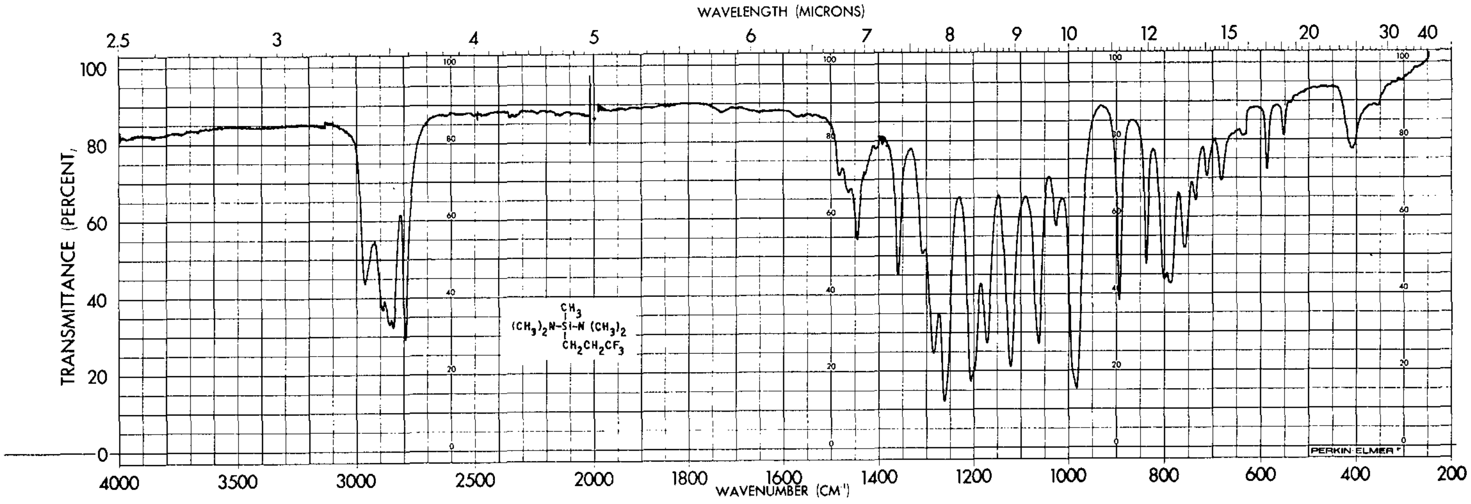

Figure 55. Infrared spectrum of bis(dimethylamino)methyl(3,3,3-trifluoropropyl)silane

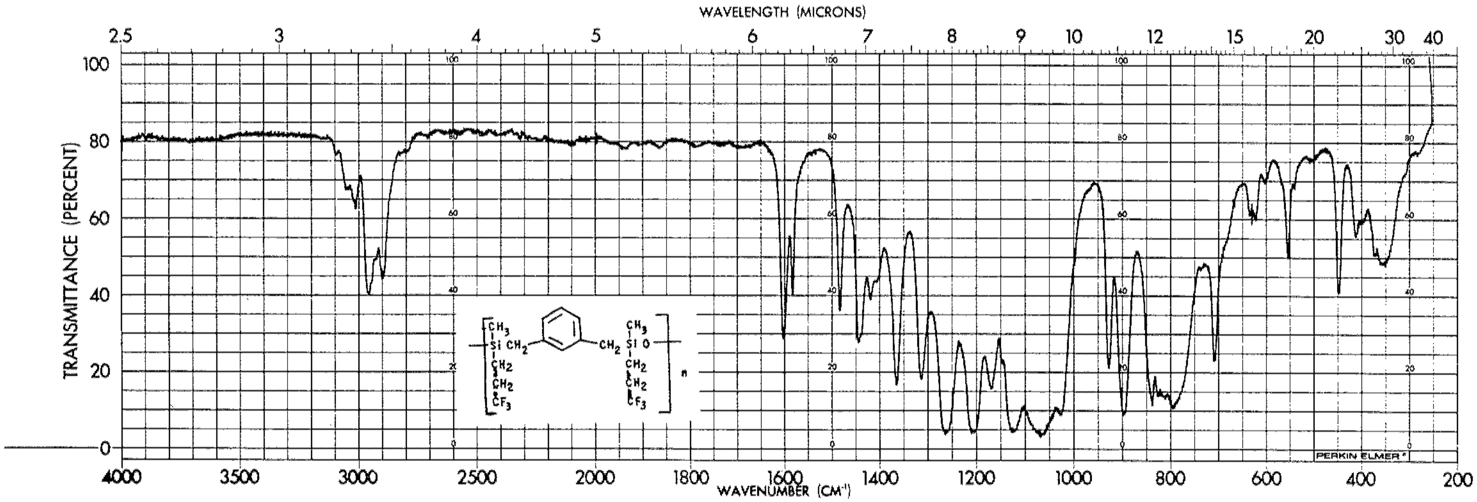

Figure 56. Infrared spectrum of poly[1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxanylene-m-xylylene]

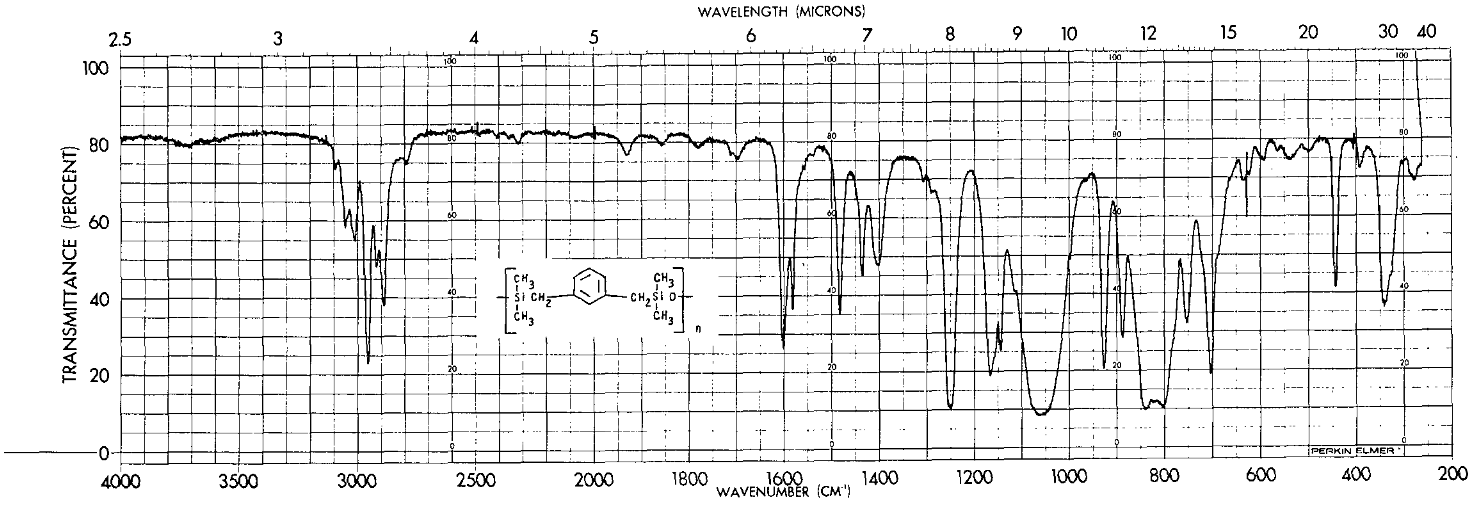

Figure 57. Infrared spectrum of poly(1,1,3,3-tetramethyldisiloxanylene-m-xylylene)

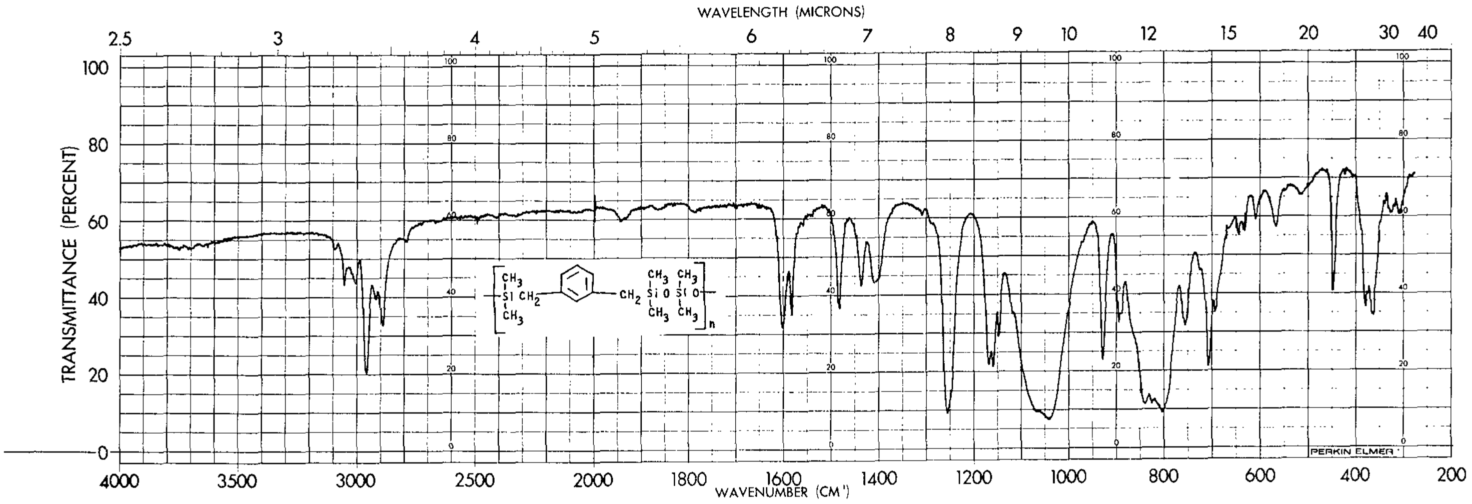

Figure 58. Infrared spectrum of poly(1,1,3,3,5,5-hexamethyltrisiloxanylene-m-xylylene)

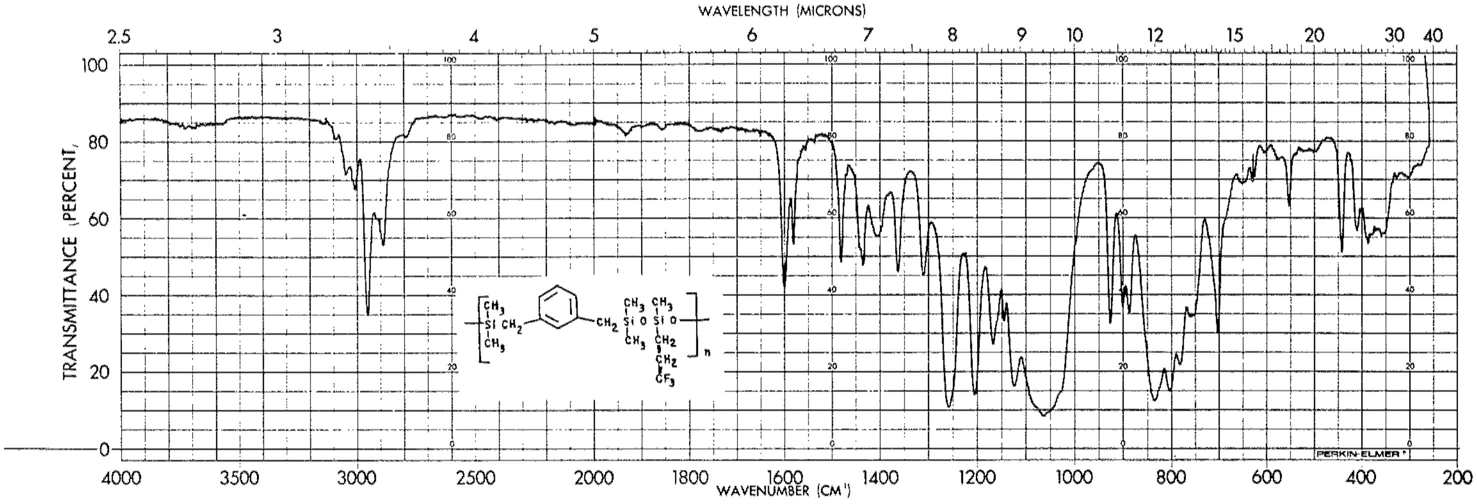

Figure 59. Infrared spectrum of poly[1,1,3,5,5-pentamethyl-3-(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]

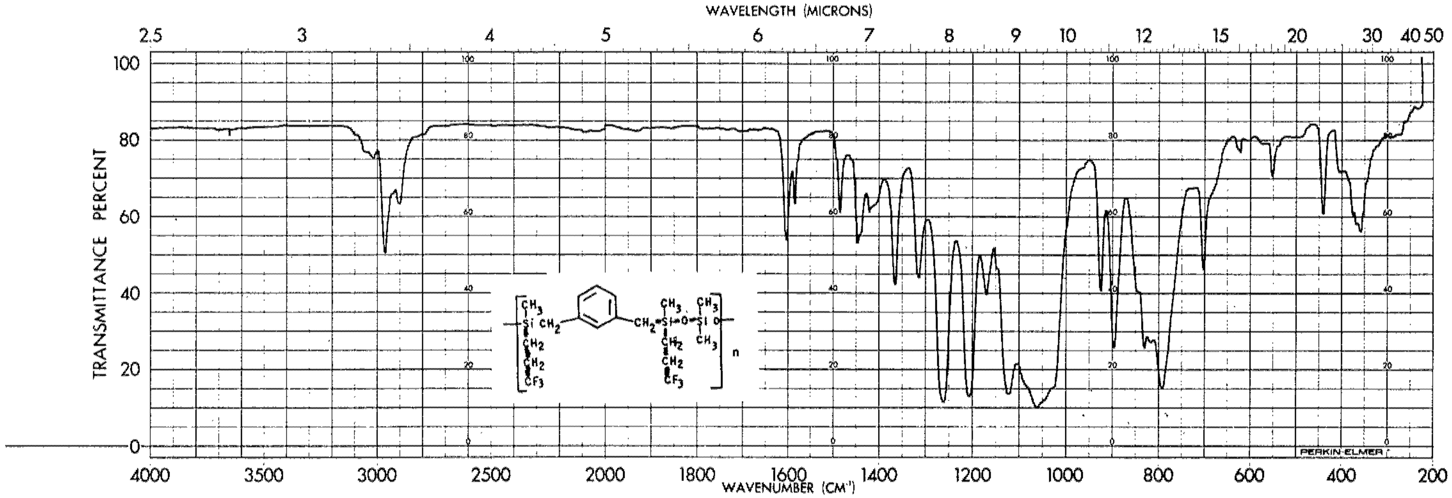

Figure 60. Infrared spectrum of poly[1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]

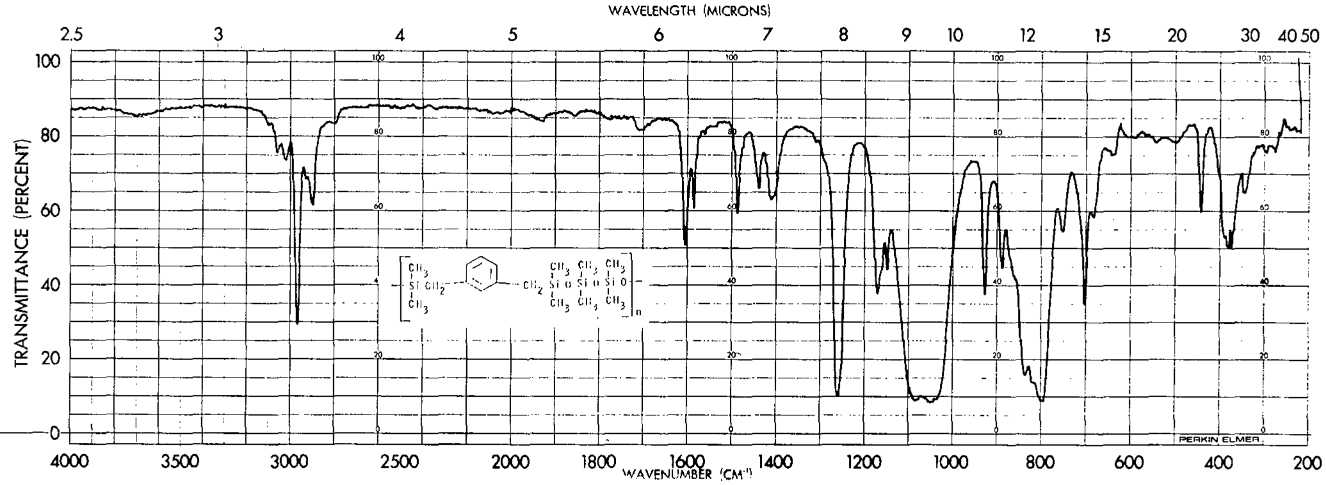

Figure 61. Infrared spectrum of poly(1,1,3,3,5,5,7,7-octamethyltetrasiloxanylene-m-xylylene)

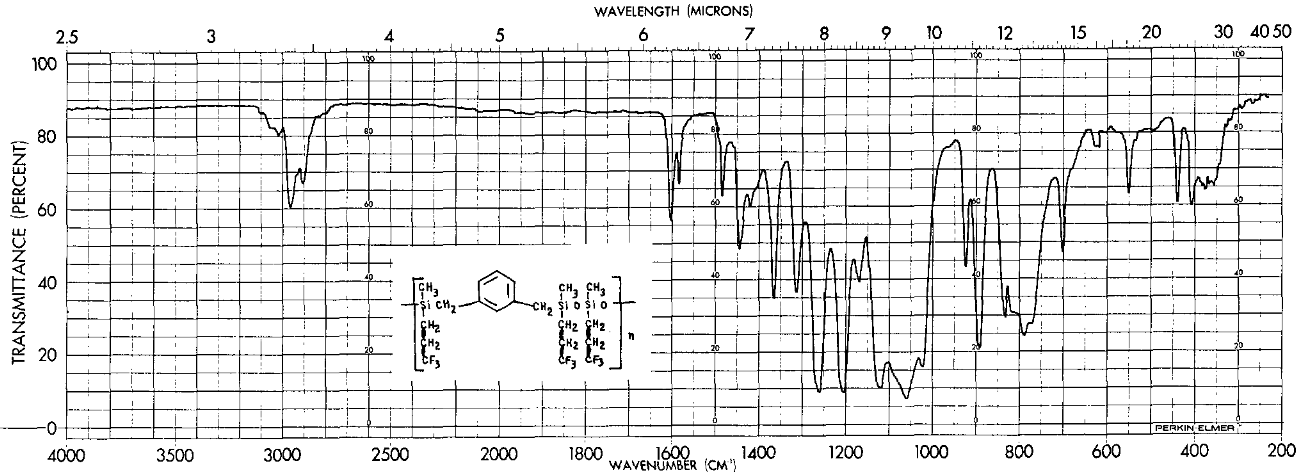

Figure 62. Infrared spectrum of poly[1,3,5-trimethyl-1,3,5-tris-(3,3,3-trifluoropropyl)trisiloxanylene-m-xylylene]

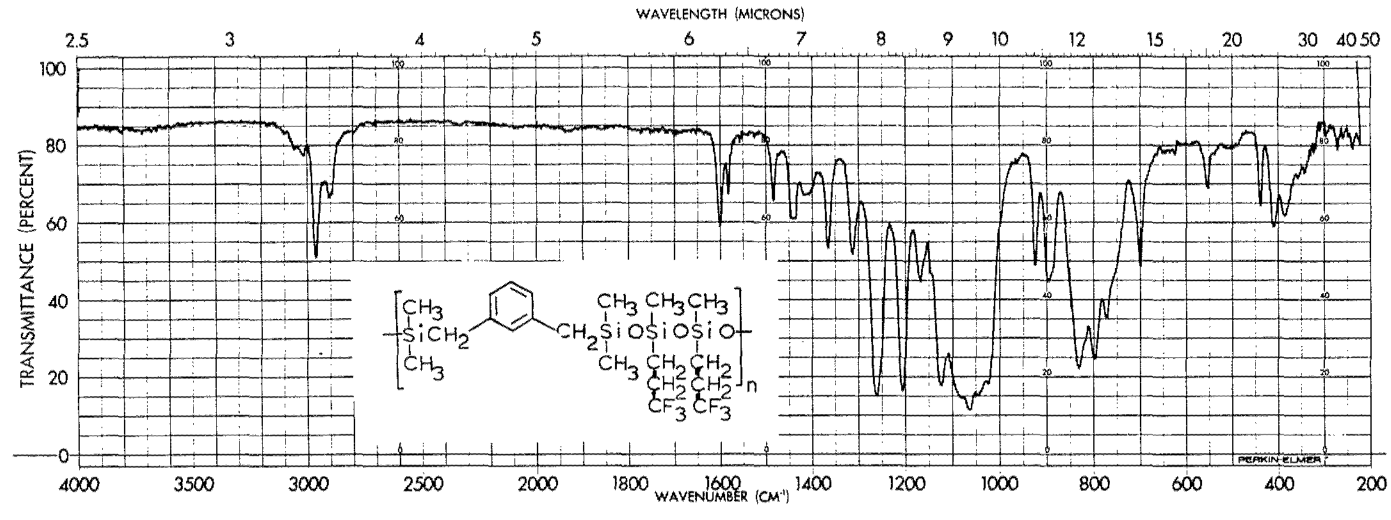

Figure 63. Infrared spectrum of poly[1,1,3,5,7,7-hexamethyl-3,5-bis(3,3,3-trifluoropropyl)tetrasiloxanylene-m-xylylene]

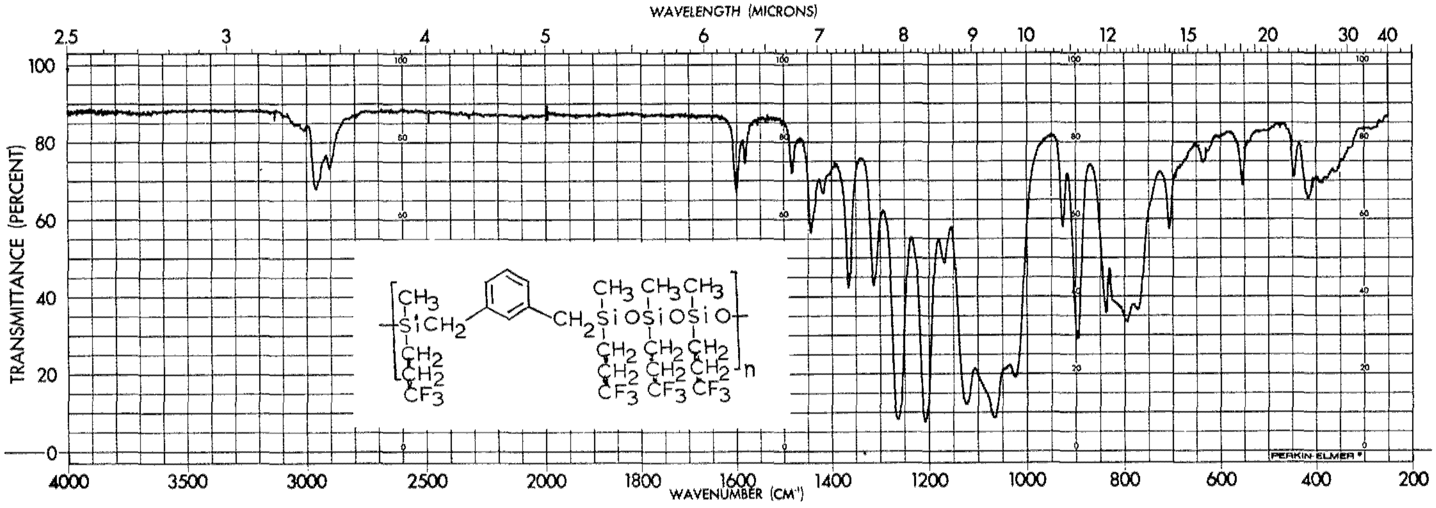

Figure 64. Infrared spectrum of poly[1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3,3,3-trifluoropropyl)tetrasiloxanylene-m-xylylene]

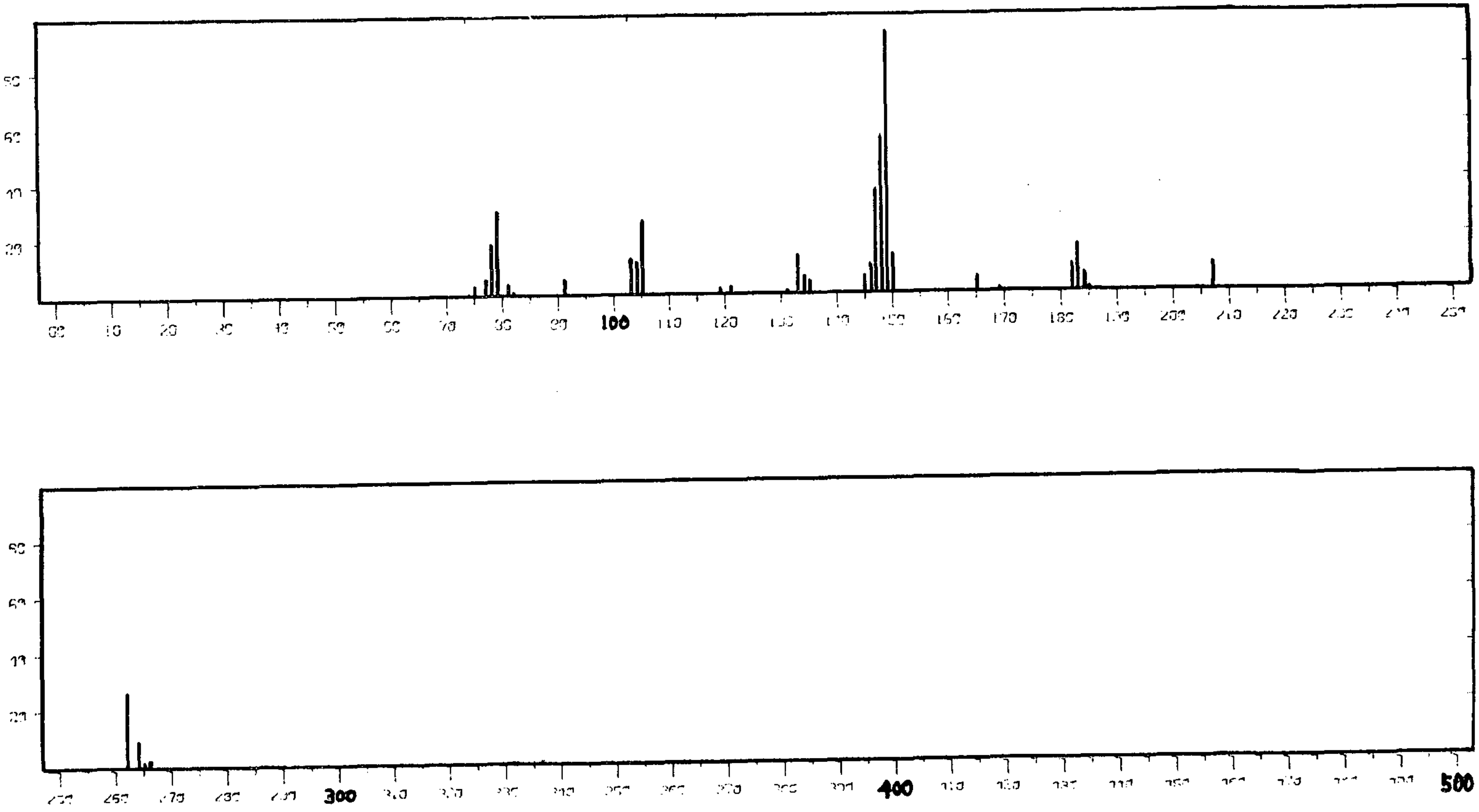

Figure 65. Mass spectrum of α,α'-bis(chloromethylsilyl)-m-xylene

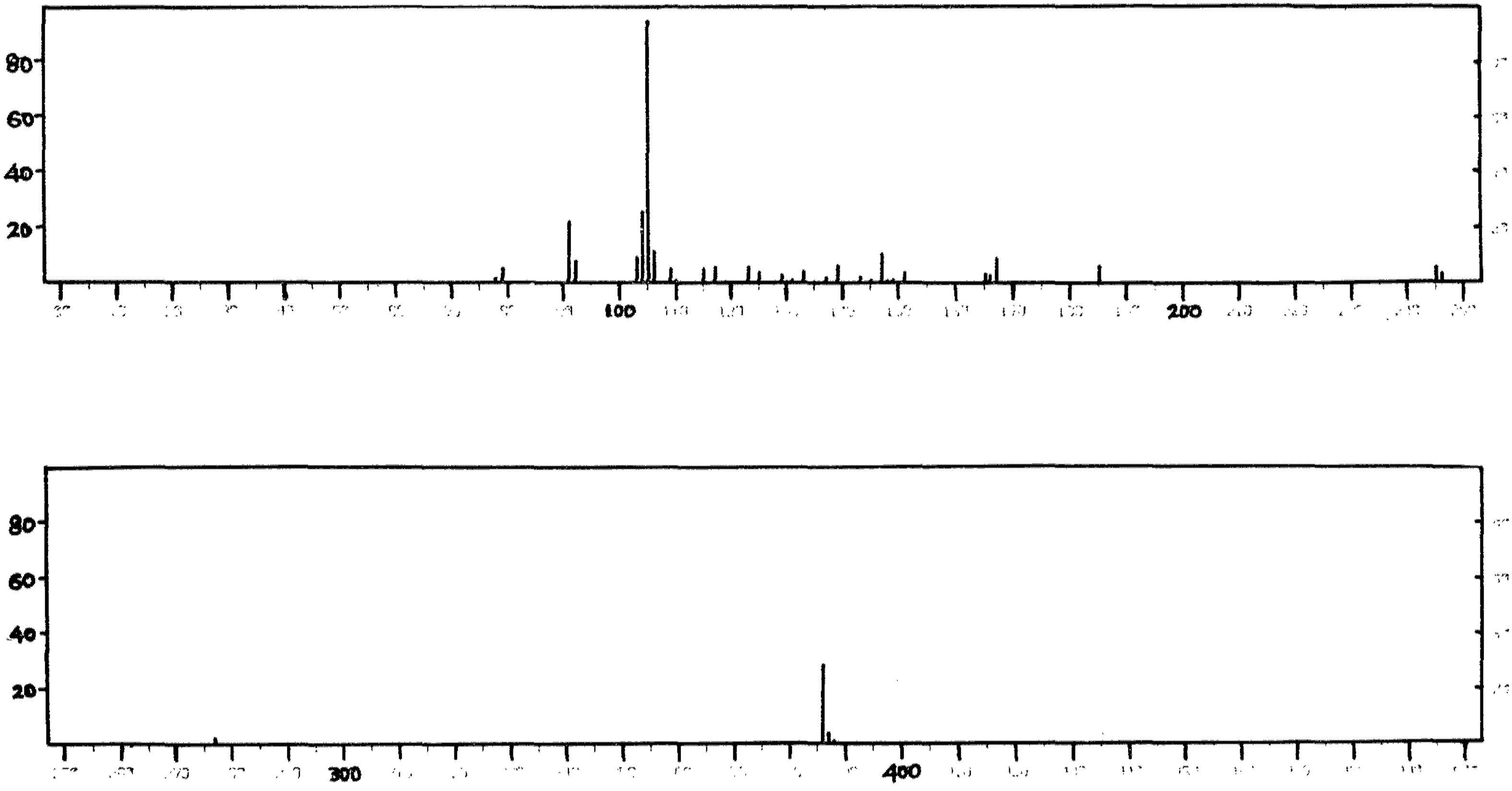

Figure 66. Mass spectrum of α,α´-bis(methyl(3,3,3-trifluoropropyl)-silyl]-*m*-xylene

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