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ARYLENESILOXANE POLYMERS FOR USE AS HIGH-TEMPERATURE AIRCRAFT INTEGRAL FUEL TANK SEALANTS

Part III Synthesis And Properties of Fluoroalkylarylene-Siloxanylene (FASIL) High-Temperature Polymer

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

DECEMBER 1978

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

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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Channel sealants
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Arylenesiloxanylenes

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

The requirement for new chemical-resistant, viscoelastic polymers with use temperatures exceeding the limits of current materials, particularly for integral fuel tank sealants, has led to the synthesis and characterization in this laboratory of a class of fluoroalkyl-substituted arylenesiloxanylene (FASIL) polymers, I, with the general structure $\text{[}SiCH_3(R_1)\text{-}1,3\text{-}C_6H_4\text{-}SiCH_3(R_2)O((SiCH_3\text{-}(R_3)O))_x\text{]}_n$, where $R_1 = R_2 = CH_3$ or $CF_3CH_2CH_2$; $R_3 = CF_3CH_2CH_2$ or CH_3; and $x = 0, 1$ or 2. Representative members of this class were synthesized from

1,3-bis(hydroxydialkylsilyl)-m-phenylenes by homopolymerization, as well as cocondensation reactions with bis-aminosilanes and disiloxanes or with the corresponding diacetoxy derivatives. A polytetrasiloxanylene (I, $x = 2$, and $R_1 = R_2 = R_3 = (CF_3CH_2CH_2)$ has been found to offer considerable promise as a candidate base material for the formulation of a non-curing, reversion-resistant, -65°F to 450°F fuel tank channel sealant with long-term utility. Formulation and laboratory evaluation studies indicate the polymer (to which the acronym FASIL has been assigned) to be superior to state-of-the-art and current candidate aircraft fuel tank sealant polymers. The potential of FASIL for use in filleting sealants as well as seal applications is indicated.

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 1978.

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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

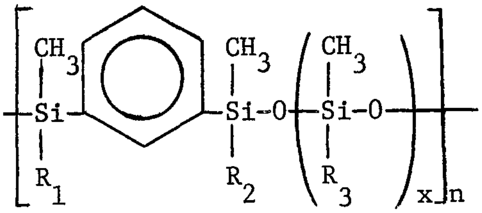
The discovery of new polymeric materials for sealant and seal applications with inherently wider use temperature range, greater chemical stability and longer operational life than state-of-the-art elastomers has proven to be an unyielding challenge to the Air Force for over a decade. Of particular concern has been the need for new viscoelastic polymers with the requisite chemical/fuel resistance, high-temperature stability, low-temperature flexibility, adhesion to metal substrates and ready processability for improved aircraft integral fuel tank sealants with broad temperature capability. The background, requirements and status of research programs aimed at this specific materials objective, with an emphasis on filleting sealants, was reviewed recently.[1]

The objective of current research in this area conducted in-house by the Polymer Branch, Air Force Materials Laboratory, has been the synthesis and evaluation of new thermally-stable organosilicon polymers as base materials for high-temperature aircraft integral fuel tank sealants with a long service lifetime (up to 10,000 hours) over a wide temperature range (from $< -40^{\circ}F$ to $500^{\circ}F$). Desired chemical and physical properties for a high-temperature aircraft sealant include long-term thermal stability ($>450^{\circ}F$), resistance to reversion at elevated temperatures in confined environments, a moderately low glass-transition temperature ($< -40^{\circ}F$ and, preferably, $-65^{\circ}F$), excellent resistance to swell by jet fuels such as JP-4 and JP-7, excellent adhesion and non-corrosivity to aircraft metallic substrates, and the capability for room-temperature cure. Oxidative stability of candidate polymers, while highly desirable, is not considered of primary significance for this application because aircraft sealants are generally intended for use under a nitrogen and fuel environment in the absence of oxygen. It was also desired to provide candidate polymers with cost advantages over current high-temperature sealant-type polymers which are available commercially or under development by other organizations.

This quest has now led to the synthesis and evaluation of a new high-temperature fluorine-containing organosilicon polymer, FASIL, which offers considerable promise as a candidate base material for a broad use-temperature, long-life integral fuel sealant of both the channel and filleting types. Of particular interest is the potential shown by this elastomeric polymer for the formulation of a non-curing, reversion-resistant -54°C (-65°F) to 232°C (450°F) fuel tank channel sealant with long-term utility. This development was the planned outgrowth of an extensive investigation[2,3] into the synthesis and characterization of new thermally- and chemical-resistant viscoelastic alkarylene- and arylenepolysiloxanylene polymers. Two classes of candidate polymers, methyl- and 3,3,3-trifluoropropyl-substituted poly(m-xylylenesiloxanylenes)[2,3] and the corresponding poly(m-phenylenesiloxanylenes), were selected for study as the most promising representatives of such macromolecular systems. Emphasis was placed in both types on di-, tri- and tetrasiloxanylene sub-classes since these would be the ones expected to yield polymers with the balance of physical, chemical and mechanical properties required for fuel tank sealant applications. In order to achieve the latter, it was necessary to develop appropriate structure/property correlations as a prerequisite to the specific tailoring of molecular structures. Representative members, appropriately substituted, of both polymer classes were synthesized and characterized with respect to their glass-transition temperature, thermal stability and solubility or fuel resistance. From the data obtained, required structure/property relationships were established to permit the prediction of structures with the optimum combination of properties.

The synthesis and characterization,[2,3,4] thermal behavior,[2,3,5] and solubility or fuel resistance,[3,6] of the first class of polymers, i.e., the poly(*m*-xylylenesiloxanylenes), has been reported previously. In this report some results of the investigation of the second class, i.e., the poly(*m*-phenylenesiloxanylenes), I, with emphasis on the synthesis and characterization of the fluoroalkyl-substituted members of the subclasses which led to the selection of FASIL as the candidate polymer of choice, are summarized.

I



$R_1 = R_2 = CH_3$ or $CF_3CH_2CH_2$

$R_3 = CF_3CH_2CH_2$ or CH_3

$x = 0, 1$ or 2

SECTION II

DISCUSSION

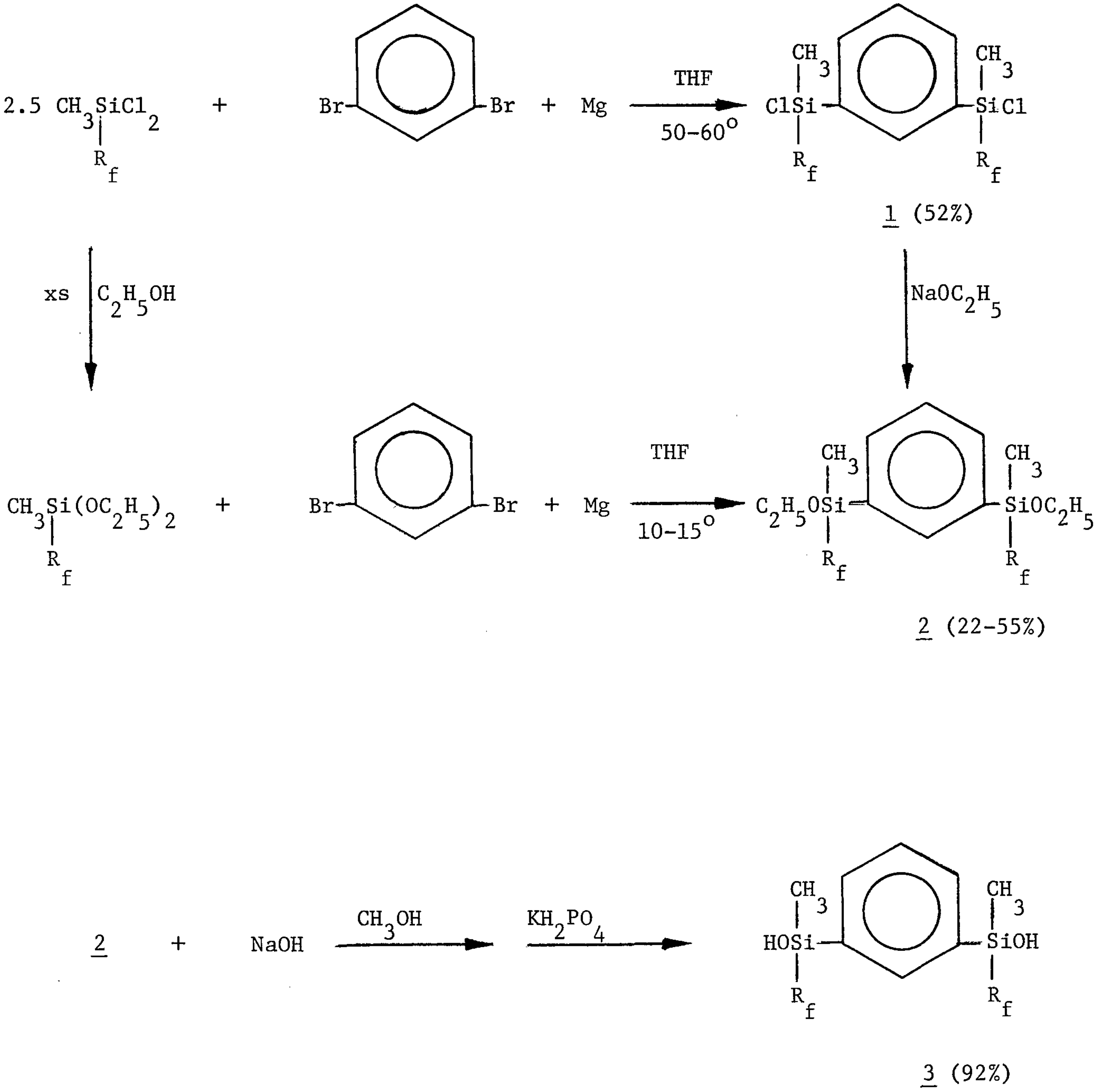
A. Synthesis of Monomers and Polymers.

As in the case of the poly(m-xylylenesiloxanylenes)[3,4] in order to obtain appropriately-structured representative members for characterization and evaluation, three subclasses or families of m-phenylenesiloxanylene polymers were considered for synthesis. These were the poly(m-phenylenedisiloxanylenes, II; -trisiloxanylenes, III; and -tetrasiloxanylenes, IV. The specific polymers in these subclasses selected for preparation were those considered likely to provide the most useful information in connection with structure/property correlations and the tailoring of the macromolecules. In order to synthesize these polymers, various methyl- and 3,3,3-trifluoropropyl-substituted 1,3-bis(silyl)benzene intermediates and monomers, including bis-chlorosilanes, bis-ethoxysilanes and bis-silanols, together with bis-aminosilanes and -disiloxanes, were initially prepared and characterized.

The synthetic sequence for the preparation of the key monomer, 1,3-bis-[hydroxymethyl-(3,3,3-trifluoropropyl)silyl]benzene (3), is shown in Scheme I. The in-situ Grignard coupling reaction of 1,3-dibromobenzene with 2.5 moles of 3,3,3-trifluoropropylmethyldichlorosilane in tetrahydrofuran afforded 1,3-bis[methyl(3,3,3-trifluoropropyl)chlorosilyl]benzene (2) in 21.6% yield. Hydrolysis of the bis-ethoxy derivative 2 with sodium hydroxide in methanol afforded a 91.5% yield of 1,3-bis[hydroxymethyl-(3,3,3-trifluoropropyl)silyl]benzene (3). An alternate procedure involving direct synthesis of the bis-ethoxy intermediate 2 from the dibromobenzene (as shown in Scheme I) provides an improved route for preparation of the monomer. By addition of methyl(3,3,3-trifluoropropyl)diethoxysilane [obtained by heating methyl(3,3,3-trifluoropropyl)dichlorosilane with an

Scheme 1

Synthesis of 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene



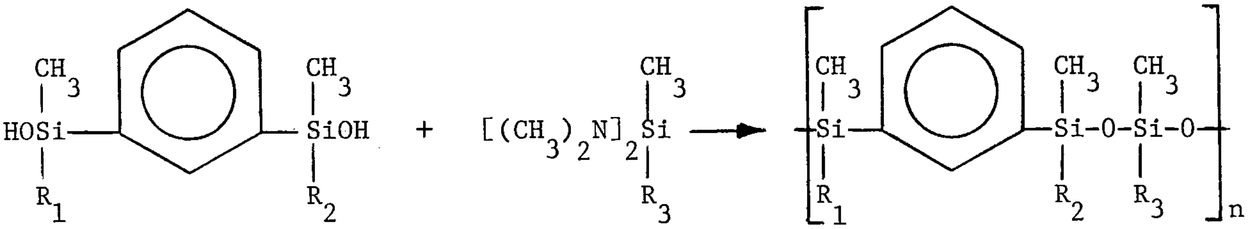
$R_f = CF_3CH_2CH_2$

excess of absolute ethanol] to the in-situ Grignard reagent from 1,3-dibromobenzene at 10-15° the bis-ethoxy derivative was obtained in overall yields (based on starting dihalide) of 50-55%. However, one difficulty with this procedure is the formation of impurities which, if not removed by extremely careful distillation,can give rise to lowered yields in the monomer synthesis and subsequent polymerization reactions.

The bis-silanols were homopolymerized in refluxing benzene, using a 1,1,3,3-tetramethylguanidine salt as catalyst, to yield the poly(m-phenylenedisiloxanylenes), II. When the two bis-silanols, 1,3-bis(hydroxydimethylsilyl)- and 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl] benzene were copolymerized with appropriately substituted bis(dimethylamino)silanes[3] (Scheme 2) or -disiloxanes[3] (Scheme 3), two families of methyl-and 3,3,3-trifluoropropyl substituted poly(m-pheylenetrisiloxanylenes), III, and -tetrasiloxanylenes, IV, were obtained. Recently, in an extension of the newly developed silanol-acetoxysilane polycondensation reaction for the synthesis of dimethyl-substituted poly(arylenesiloxanylenes)[8], it was found possible to synthesize the corresponding methyl(3,3,3-trifluoropropyl) analogs. For example, by the reaction of 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene with the appropriately-substituted diacetoxysilanes or diacetoxydisiloxanes, III($R_1 = R_2 = R_3 = R_4 = CF_3CH_2CH_2$) and IV($R_1 = R_2 = R_3 = R_4 = CF_3CH_2CH_2$) were obtained. Since a number of the newly synthesized polymers [e.g., III($R_1 = R_2 = CF_3CH_2CH_2$, $R_3 = CH_3$)] could not be cured by conventional methods to provide vulcanizates for fuel swell evaluation, vinylsilyl groups were introduced into such polymers in order to provide sites for crosslinking. This was accomplished by the addition of methylvinylbis(dimethylamino)silane as 3 mole percent of the total silylamine monomer composition in the

Scheme 2

Synthesis of 3,3,3-Trifluoropropyl-Substituted Poly(m-phenylenetrisiloxanylenes)

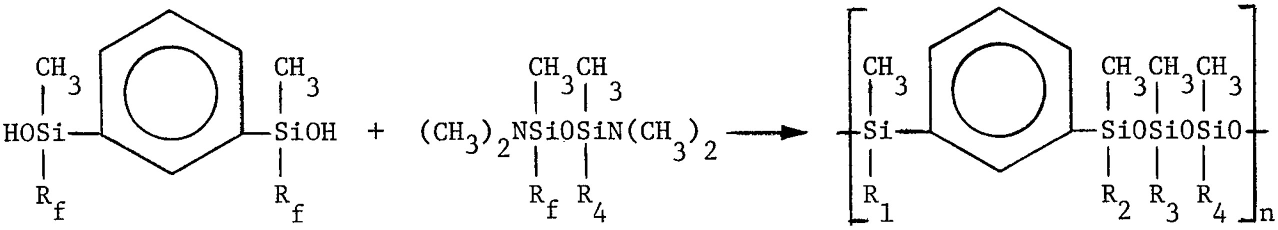


III

$R_1 = R_2 = CF_3CH_2CH_2$ or CH_3; $R_3 = R_4$ = Same as or different R_1.

Scheme 3

Synthesis of 3,3,3-Trifluoropropyl-Substituted Poly(m-phenylenetetrasiloxanylenes)



IV

$R_1 = R_2 = CF_3CH_2CH_2$ or CH_3; $R_3 = R_4$ = Same as or different R_1.

reactions shown in Schemes 2 and 3. The vinyl groups incorporated in the resulting polymers would be expected to be distributed randomly along the chains.

B. Physical Properties of Polymers.

The synthesized polymers, as with their m-xylylene analogs, were fully characterized and evaluated with respect to glass-transition temperature, thermal stability and fuel resistance or polymer insolubility. Viscosities, together with number average molecular weights obtained by either vapor phase or membrane osmometry, were recorded for the relatively low molecular weight polymers sought. Glass-transition temperatures were determined by means of differential scanning calorimetry (DSC), with $\Delta T = 20^{\circ}C/min.$, and have been reported in part[9]. Thermal characterization of the polymers involved thermogravimetric analysis (TGA) under vacuum at $\Delta T = 5^{\circ}C/min.$ Data obtained from the TGA curves, including values of T_{25} (temperature at which 25% weight loss is recorded), were discussed for certain of the polymers, together with that for their m-xylylene analogs, in an earlier report[3,5]. In order to determine fuel resistance, polymers were first cured with di-t-butylcumyl peroxide at 170°C and 2000 psi. In the case of those polymers with a high content of fluoroalkyl groups, samples of polymers containing the aforementioned 3 mole percent of vinyl groups were used for preparation of the volcanizates. Volume swell ratios of the volcanizates were determined after immersion of the samples for 72 hours at room temperatures in hydrocarbons, such as isooctane and JP-4 jet fuel[3]. The results obtained with regard to the solvent resistance of the polymers through the use of vulcanizates has been corroborated in part in studies on solvent interactions with both the m-xylylene and, to a lesser extent, the m-phenylenesiloxanylene polymers. Using gas-liquid chromatography (GLC) to determine infinite dilution activity coefficients, structure/solubility relationships were derived which correlated well with volume swell data on volcanizates[6].

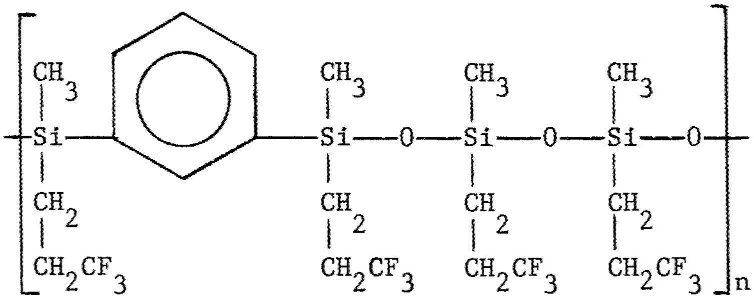
From the results obtained and structure/property correlations[3,4,5,6] previously established in our investigation of their m-xylylene analogs, it was possible to reduce the total number of polymer(m-phenylenesiloxanylenes) required for synthesis and property evaluation. More specifically, from the earlier fuel resistance/polymer solubility studies, a fluorine content of 30% or greater by weight appeared necessary to provide required fuel resistance to the polymer systems under investigation. Therefore, in the poly(m-phenylenesiloxanylenes) only those polymers with a high ratio of 3,3,3-trifluoropropyl to methyl substituents could be expected to possess desired fuel resistance. Thus, the only members of this class with potential for fuel tank sealants were further restricted to five in number, consisting only of those with two or more fluoroalkyl groups per mer unit. Further detailed evaluation of this smaller group of polymers in both uncured and cured states and with emphasis on isothermal aging and solvent resistance at elevated temperatures was then carried out. This resulted in the final selection of poly[m-phenylene-1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3,3,3-trifluoropropyl)tetrasiloxanylene] as the most promising member not only of the group but of both classes of polymers investigated.

The aforementioned fluoroalkylarylenesiloxanylene polymer, IV(R_1 = R_2 = R_3 = R_4 = $CF_3CH_2CH_2$) has been given the name FASIL, an acronym derived from the general polymer class name. In addition to being readily synthesized from commercially-available starting materials (cf. Experimental), the polymer was found to exhibit a better overall combination of requisite physical, chemical and mechanical properties for fuel-resistant sealant applications than any of the newly synthesized siloxanylene or other candidate sealant polymers (Table I).

Table I

FASIL* SEALANT POLYMER

Structure:



Properties:		FASIL	SOA$^+$
Viscosity, η,	=	0.02-0.33	
Wt. Loss, 400°F, 190 hr.	=	3%	5%
T_{25} (TGA)	=	415°C (779°F)	
T_g	=	-49°C (-57°F)	-28°F
Wt. Gain, JP-4, 72 hR, Rt	=	9.7%	20.1%

*FASIL = MBP ACRONYM FOR FLUOROALKYLARYLENESILOXANYLENE

+IMPROVED STATE-OF-THE-ART CANDIDATE POLYMER

C. Evaluation of FASIL.

Additional quantities of FASIL were synthesized for use in formulation and evaluation studies as a fuel tank channel sealant. Preliminary results of FASIL evaluation as a formulated sealant, including accelerated broad-temperature range cycling tests from -54°C(-65°F) up to 232°C (450°F) and titanium stress corrosion testing, indicate that FASIL possesses superior properties (Table II) and life expectancy (Table III) to other elastomeric polymers evaluated as a candidate for a wide-temperature range fuel tank channel sealant material. In addition to holding promise as a channel sealant polymer, structural modification of FASIL as a two-part system is expected to

Table II

PROPERTIES OF FASIL REQUIRED FOR BROAD-TEMPERATURE FUEL TANK SEALANTS

MAJOR	MINOR
● Long-Term Thermal Stability [Up to 260°C (500°F)]	● Reversion Resistance [204°C (400°F), 7 days-TOTAL]
● Low-Temperature Flexibility [-54°C (-65°F]	● Extrudable
● Excellent Adhesion to Al & Ti	● No Stress Corrosion on Ti Substrates
● Chemical Stability High Resistance to JP-4 Fuel Nonhydrolyzable	● Reasonable Cost Synthesis Based on Commerc.-Available Starting Materials

permit its use for the formulation of filleting sealants. Under contract, FASIL-type vinyl-terminated oligomers, chain extenders and crosslinking agents are now being synthesized to enable the early development of a FASIL-based filleting sealant. Lastly, from the properties obtained in the evaluation of its vulcanizates, FASIL offers further potential as a base polymer for chemical-resistant seal applications.

TABLE III

PRELIMINARY EVALUATION OF FASIL & OTHER CHANNEL SEALANTS - ACCELERATED AGING

CYCLING UNDER 20 PSI FUEL (JP-4) PRESSURE

SEALANT	8 HRS AT 320°F. 16 HRS COOLING TO R.T.		8 HRS AT 350°F. 16 HRS COOLING TO -65°F.		8 HRS AT 450°F. 16 HRS COOLING TO R.T.	
	CYCLES/HRS	CONDITION	CYCLES/HRS	CONDITION	CYCLES/HRS	CONDITION
FLUOROSILICONE (DC-94-031)	5/120	FAILED (EXTRUSION)	STATE	OF	THE	ART
FLUOROSILICONE C-94-011-MODIF.)	----	----	20/480	FAILED (REVERSION)	----	----
HYBRID FLUOROSILICONE (FCS-210)	----	----	20/480	PASSED	2/48	FAILED
ARYLENESILOXANE (FASIL)	20/480	PASSED	20/480	PASSED	3/72	PASSED

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 Perkin-Elmer Model 21 or a Beckmann Model IR-33 spectrophotometer.

Nuclear magnetic resonance, and infrared 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^o per minute from 120^o to 300^o, 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 and Monomers.

1. <u>1,3-Bis(3,3,3-trifluoropropylmethylchlorosilyl)benzene</u>

To a mixture of magnesium (4.8 g., 0.2 g-atom) and methyl-3,3,3-trifluoropropyldichlorosilane (52.7 g., 0.25 mole) in tetrahydrofuran (50 ml.)

was added dropwise under nitrogen a solution of m-dibromobenzene (23.6 g., 0.1 mole) in tetrahydrofuran (50 ml.) over a two-hour period. The addition was controlled to maintain a temperature range of 50-60°. The resulting mixture was then heated under reflux for 16 hours and, after adding 200 ml. of n-hexane to the mixture, inorganic solids were filtered. Fractional distillation of the filtrate gave 22.2 grams (52%) of crude 1,3-bis(3,3,3-trifluoropropylmethylchlorosilyl)benzene, bp 169-174°/3 Torr.

2. 1,3-Bis[ethoxymethyl-(3,3,3-trifluoropropyl)silyl]benzene

A solution of sodium ethoxide, prepared from 2.76 grams of sodium and 300 ml. of absolute ethanol, was added slowly under nitrogen into 25.6 grams (0.06 moles) of 1,3-bis(3,3,3-trifluoropropylmethylchlorosilyl)benzene. The reaction mixture was heated under reflux for 15 minutes and then cooled to room temperature. Ethanol was removed on a rotary evaporator to leave a residue which was transferred into a smaller flask with the aid of diethyl ether. Fractional distillation of the residue gave 5.8 grams (21.6%) of 1,3-bis-[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene, bp 113.5-114.5°/0.03 Torr; mass spec (290 eV) m/e 446, 427.

3. 1,3-Bis[hydroxymethyl-(3,3,3-trifluoropropyl)silyl]benzene

To the stirred mixture of 2.6 grams of sodium hydroxide, 11 ml. of methanol and 1.2 ml. of water, was added 7 grams (0.0157 moles) of 1,3-bis-[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene, followed by the addition of a mixture of 2.6 grams of sodium hydroxide and 12 ml. of water. The resulting mixture was stirred for 30 minutes and then poured into a solution of 17 grams of potassium dihydrogen phosphate of 320 grams of water and ice. Diethyl ether was used to extract the oily product. The ether extract was washed with water, dried over anhydrous magnesium sulfate and evaporated on a rotary evaporator.

Fractional distillation of the clear oily residue through a short-path distillation column gave 5.6 grams (91.5%) of the desired 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene, bp 140-142°/0.1 Torr; nmr (CCl_4, external TMS) δ 0.285 (s, 6, $SiCH_3$), 0.667-1.17 (m, 4, $SiCH_2$), 1.33-2.42 (m, 4, CCH_2), 4.14 (s, 2, OH) and 7.0-7.84 (m, 4, ArH); F^{19} nmr (CCl_4, External $CFCl_3$) -3860 Hz. (t, CF_3); mass spec (290 eV) m/e 390; molecular weight (benzene, VPO) 383, 394 (theory 390). Calc'd for $C_{14}H_{20}F_6O_2Si_2$: C, 43.06; H, 5.16; F, 29.19; Si, 14.39. Found: C, 43.57; H, 5.29; F, 31.44; Si, 15.08.

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

This monomer was prepared by the procedure described in a previous report.[3,7]

5. 1,3-Dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

The disiloxane intermediate was obtained using a modification[3] of the literature procedure.[10]

6. 1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-disiloxane

This monomer was synthesized by the procedure described by the authors in earlier publications.[3,7]

C. Synthesis of Polymers.

The synthesis of the m-phenylenesiloxanylene polymers was carried out by a general procedure which is best illustrated by the two examples (including that for FASIL) outlined below.

1. Poly[m-phenylene-1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)-trisiloxanylene]

Into a 100-ml. three-necked flask, equipped with thermometer, stirrer, nitrogen inlet, and condenser connected to a solution of hydrochloric acid, were placed 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene (3.9g, 0.01 mole), 1.33g (0.01 mole) of bis(dimethylamino)dimethylsilane and 5 ml. of toluene. The mixture was warmed to 110° and dimethylamine began to evolve when the temperature reached 85° . After 15 minutes of heating the remainder of the diaminosilane, 0.15g, was added dropwise over a period of 5 minutes. The mixture was heated for an additional 1.5 hours (or for a total of two-hours reaction time) and then hydrolyzed with 1.5 ml. of water. Water was removed as an azeotrope. The polymer was dissolved in 50 ml. of toluene, filtered, precipitated with 50 ml. of methanol, washed twice with 30 ml. of methanol, and dried at 260° and 0.8 Torr for 16 hours to yield 3.0 grams of poly[m-phenylene-1,3,3,5-tetramethyl-1,5-bis(3,3,3-trifluoropropyl)trisiloxanylene] as a translucent, viscous gum, molecular weight (VPO in benzene) 9,310; η_{inh} = 0.04 dl/g.

2. Poly[m-phenylene-1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3,3,3-trifluoropropyl)tetrasiloxanylene] with vinyl groups.

Into a 100-ml. three-necked flask, equipped with thermometer, stirrer, nitrogen inlet, and condenser which was connected to a solution of hydrochloric acid, was placed 5.0 grams (12,8 mmoles) of 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene, 4.275 grams (11.16 mmoles) of 1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)-1,3-bis(dimethylamino)disiloxane, 54.9 mg (0.36 mmoles) of methylvinylbis(dimethylamino)silane, and 5 ml. of toluene. The mixture was warmed to 110° during which period dimethylamine began to evolve. After 15 minutes of warming, the remainder of the diaminosilanes, 0.475 grams (0.12 mmoles) of 1,3-dimethyl-1,3-bis-(3,3,3-trifluoropropyl)-1,3-bis(dimethylamino)disiloxane and 6.1 mg (0.04 mmoles) of methylvinylbis-(dimethylamino)-silane, was added dropwise over a period of 5 minutes. The mixture was heated for 1.5 hours (or for a total of two-hours reaction time) and then hydrolyzed with 1 ml. of water. Water was removed as an azeotrope. The polymer was dissolved in 3 ml of toluene, filtered, precipitated with 15 ml. of methanol, washed twice with 30 ml. of methanol, and dried at 260° and 0.1 Torr for 16 hours to yield 4.2 grams of poly[m-phenylene-1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3,3,3-trifluoropropyl) tetrasiloxanylene](with 3 mole percent of vinylmethylsiloxy groups incorporated randomly onto the polymer backbone) as a very viscous oil, molecular weight (VPO in THF) 3,700; Tg (DSC, $\Delta T = 20^\circ$/min.) $-49^\circ C$; transparent; $\eta_{inh} = 0.02$ dl/g.

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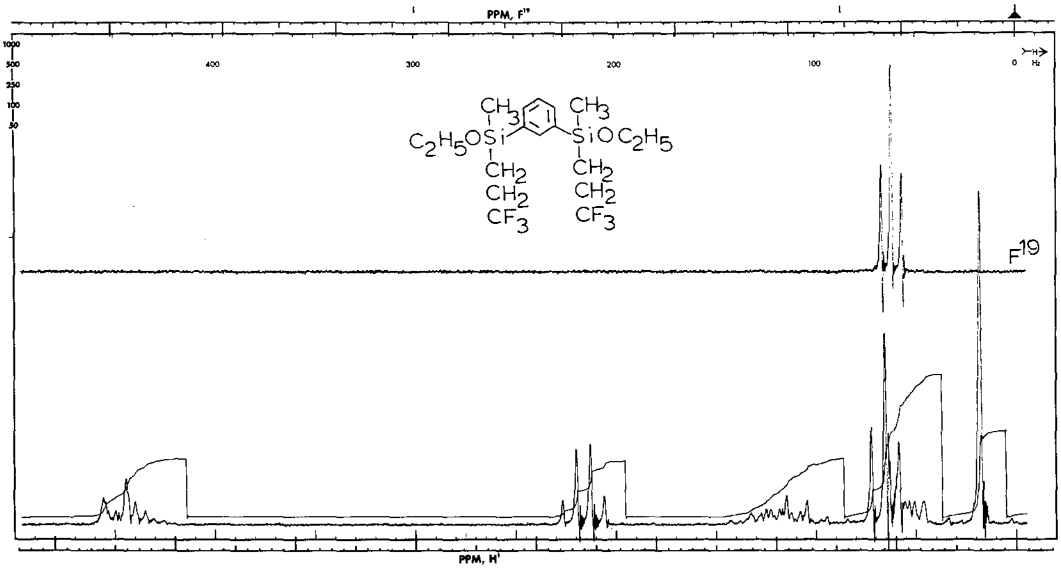

Figure 1. NMR spectrum of 1,3-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene

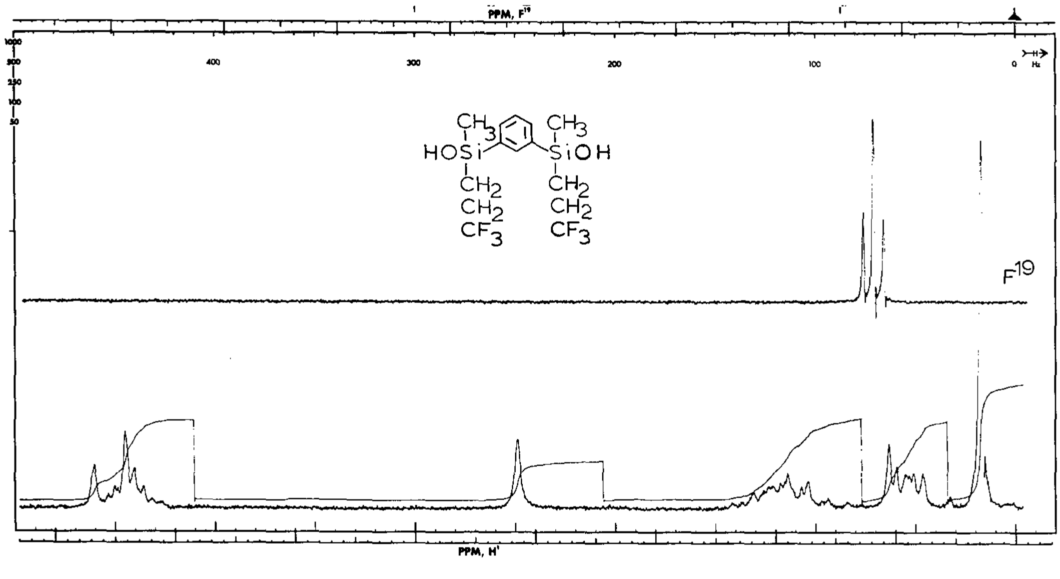

Figure 2. NMR spectrum of 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl(silyl]benzene

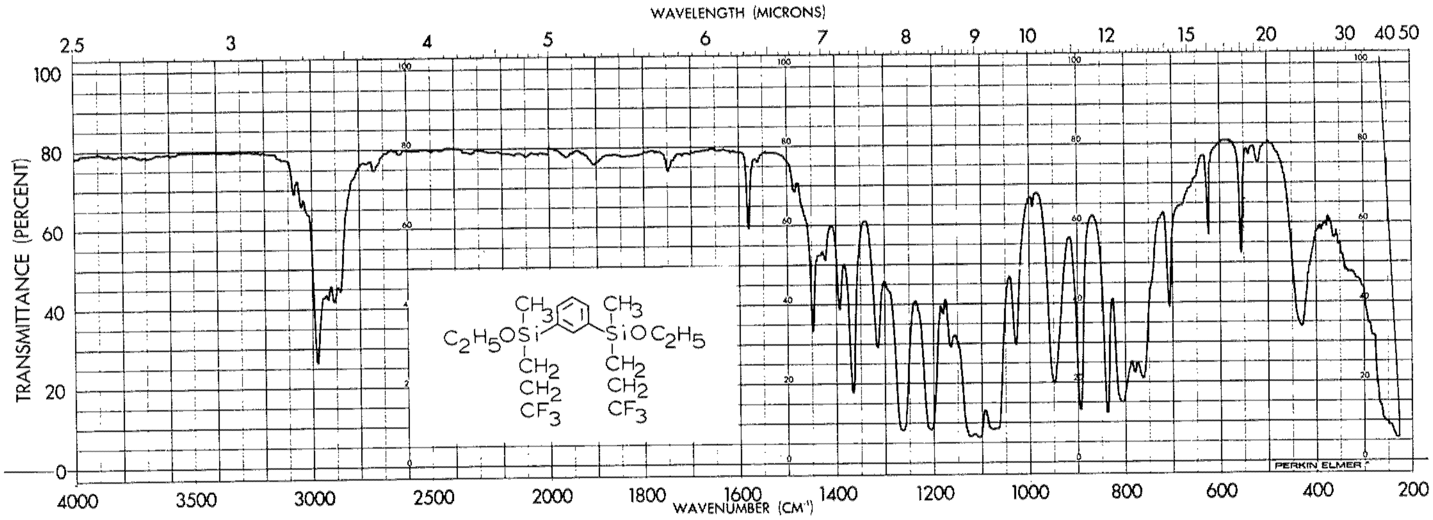

Figure 3. Infrared spectrum of 1,3-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene

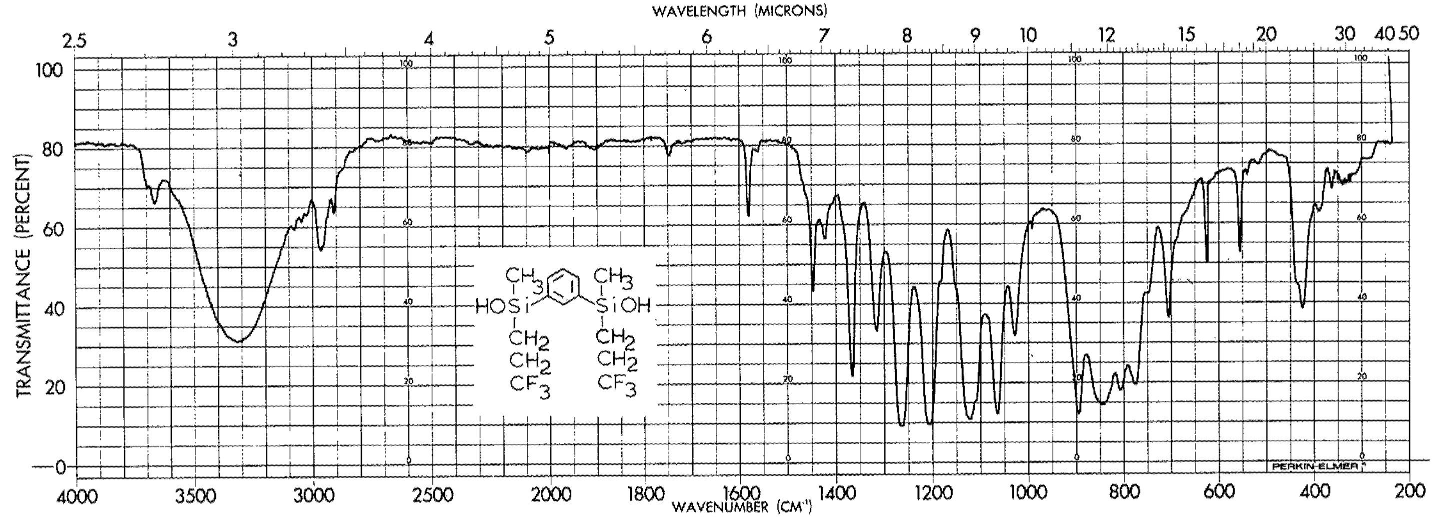

Figure 4. Infrared spectrum of 1,3-bis[hydroxymethyl(3,3,3-trifluoropropylsilyl]benzene

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