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FLUOROALKYL SILOXANES AS LIQUID-REPELLENT FABRIC FINISHES, PART I

A STATE-OF-THE-ART REVIEW AND SYNTHESIS OF THE MONOMERS

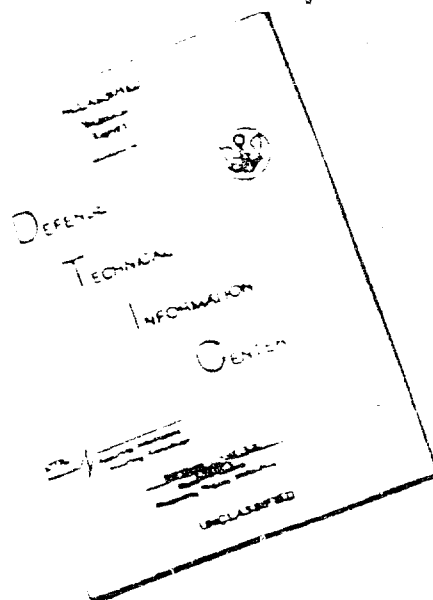
by
A.W. Bovenkamp



PROJECT NO.
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JUN 1979
OTTAWA

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FLUOROALKYL SILOXANES AS LIQUID-REPELLENT FABRIC FINISHES
PART I
A STATE-OF-THE-ART REVIEW AND SYNTHESIS OF THE MONOMERS

by

J.W. Bovenkamp

Environmental Protection Section
Protective Sciences Division

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ABSTRACT

This project concerns the evaluation of fluoroalkyl-substituted siloxane polymers as liquid-repellent finishes. First, a brief literature review is given on the current state of the art of these finishes. Second, syntheses and properties for a family of ten fluoroalkyl silanes are reported. These monomers include the best of those utilized in the literature as well as several new ones chosen to elucidate the effect of structure on liquid repellent properties. A second report will describe the method of polymerization, the liquid repellency values obtained with the homopolymers, and the results of copolymerizations with the much cheaper non-fluorinated silanes.

RÉSUMÉ

Le présent projet se rapporte à l'évaluation des polymères siloxanes, contenant des substituants fluoroalkyles, comme finis hydrofuges et oléofuges. Premièrement, on passe brièvement en revue la littérature concernant ces finis. Deuxièmement, on présente les synthèses et les propriétés d'une famille de dix fluoroalkylsilanes. Ces monomères incluent les meilleurs de ceux mentionnés dans la littérature, de même que plusieurs nouveaux monomères sélectionnés pour élucider l'influence de la structure sur les propriétés hydrofuges et oléofuges. Un second rapport décrira la méthode de polymérisation, le degré d'imperméabilisation obtenu avec les homopolymères et les résultats de copolymérisations avec des silanes non-fluorés moins chers.

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INTRODUCTION

Oil and water repellency are important commercial properties. Prior to the 1960's water repellency had been provided by such materials as waxes, pyridinium-type repellents, and by methyl- and dimethylsiloxanes (1,2). It was not until the 1960's that the use of fluorochemicals to provide both oil and water repellency became possible. A pioneering paper in this regard was that of DeMarco et al. (1) which described a combination application of a pyridinium-type repellent with a fluorocarbon to give a durable finish with excellent water repellency and a certain degree of oil repellency (a standard test was not yet available). In the mid 1960's, a series of patents was issued to E.I. du Pont de Nemours and Company on the use of fluoroalkyl-substituted acrylates and methacrylates as polymeric water and oil repellents. There is still a high commercial demand for these compounds (3).

Several patents have been issued, mostly during the last decade, on the use of fluoroalkyl-substituted siloxanes as oil-and water-repellent finishes (4-9). As far as we are aware, these patents have not been exploited commercially. It is the purpose of this project to evaluate the fluoroalkyl-substituted siloxanes as liquid repellents. It is important to clarify the differences between patents in which essentially all of this work is found and results reported in scientific papers. Also, the relationship between the actual commercial formulations and the patent must be explained. The structures of the materials used in the commercial formulations are proprietary information and are kept secret. The finishes are marketed under trade names. The patent literature is usually the only means of obtaining information on these formulations. However, because of the nature of patents (10), it is often difficult to obtain anything more than general information. Patents differ from scientific papers in several ways (10). A patent is a legal document and legal terminology is used. A patent disclosure is "broadened" to include all materials, conditions, and procedures which the applicant and his attorney believe to be equally likely to be "operative" in order to protect all the ways in which the invention might be applied. Thus, there is a risk that some of the ways of practicing the invention, as outlined in the patent, might prove, on trial, to be inoperative. In addition, not all examples cited in patents describe experiments that were actually run, but instead provide the inventor's teaching of how they should best be run. Finally, the best way to practice the invention is not always specifically highlighted and this must be determined.

These considerations indicate that it would be very difficult or impossible in the evaluation of fluoroalkyl-substituted siloxanes to compare the results reported in one patent using one set of structures with those reported in another patent using a different set of structures. Variations

Table I. Structures and Numbering System of the Silane Monomers

$\text{CF}_3(\text{CF}_2)_8\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	<u>1</u>
$\text{CF}_3(\text{CF}_2)_8\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_2\text{CH}_3$	<u>2</u>
$\text{CF}_3(\text{CF}_2)_6\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	<u>3</u>
$\text{CF}_3(\text{CF}_2)_6\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	<u>4</u>
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	<u>5</u>
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	<u>6</u>
$(\text{CF}_3)_2\text{CFO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	<u>7</u>
$(\text{CF}_3)_2\text{CFO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	<u>8</u>
$(\text{CF}_3)_3\text{CO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	<u>9</u>
$(\text{CF}_3)_3\text{CO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	<u>10</u>

in polymerization methods, weight of finish applied, test methods, and curing times and temperatures are further complicating factors. Also, monomers with promising structures were not tested. It was decided to synthesize a series of ten monomers having the widely varying structures shown in Table I. Some of these monomers, as will be indicated later, have been utilized previously in the above-mentioned patents while others have not and are new compounds. All of them are alkoxy derivatives and standardized methods of polymerization, application to fabric, and curing have been applied in an attempt to determine the effect of structure on liquid repellency.

In this report, the synthesis and properties of these monomers will be presented. A brief state-of-the-art review is also included here since a suitable one is not available in the literature. In Part II, the polymerization methods, curing conditions, and liquid-repellent properties imparted to nylon/cotton and cotton by the homopolymers will be reported. Also included in Part II will be a study of the effect of copolymerizing these monomers with the much cheaper non-fluorinated alkyl silanes.

A STATE-OF-THE-ART REVIEW

A. IMPORTANCE OF LIQUID-REPELLENT FINISHES TO THE MILITARY

Fluoropolymers, because of their special properties, have been and still are of great interest to the military. In fact, much of the original scientific research in the development of fluorinated substances has been either carried out at military establishments or financially supported by the military (see for example, 1, 11-17). Although fluorinated substances are finding many uses, especially in areas where low and high temperatures are necessary, our intention in this report is to concentrate on their liquid-repellent properties (as fabric finishes). It should be noted that the liquid-repellent finish is applied to the outermost "shell" fabric of the serviceman's clothing. The fabric and its finish should provide protection against both the physical and enemy-imposed environments as exemplified by chemical warfare agent liquid droplets.

The task of developing a completely effective liquid repellent would be easier if a barrier material impermeable to both air and water vapour could be used. That is, a material which contains no pores and which would be impermeable to both air and moisture vapour. Such an approach is not practical, however, because it would result in the buildup of heat and moisture inside the garment, causing, initially, excessive discomfort to the soldier and ultimately, producing a casualty by heat prostration. The ideal protective outer covering would prevent the penetration of both aqueous and organic liquids from without and yet allow the transfer of moisture vapour

from within. The present approach to this problem is to treat the outermost fabric shell with a fluorinated polymer, which because of the high fluorine content, has a low surface tension and thus prevents the entry of liquids such as water and organic liquids up to a certain surface tension. An important practical consideration, in terms of durability, is the strength of adherence of the polymer to the fabric as well as the stability of the functionality linking the fluorinated substituent to the polymer backbone.

Since fluorinated finishes are both oil and water repellent as well as relatively inert, a certain degree of protection is afforded against dissolved chemical and biological agents borne in these media. Since fluorinated siloxanes have an inorganic backbone and are heavily halogenated it is hoped that at least they would not contribute to the fire hazard and possibly some fire resistance might be imparted to the fabric. In this connection it has been found that the non-fluorinated polymer, polydimethylsiloxane, will not burn. In fact, this polymer cannot be induced to burn even when a bunsen-burner flame is applied directly to it.

B. FLUORINATED SUBSTANCES AND LIQUID REPELLENCY

(i) APPLICABLE PROPERTIES OF FLUORINE

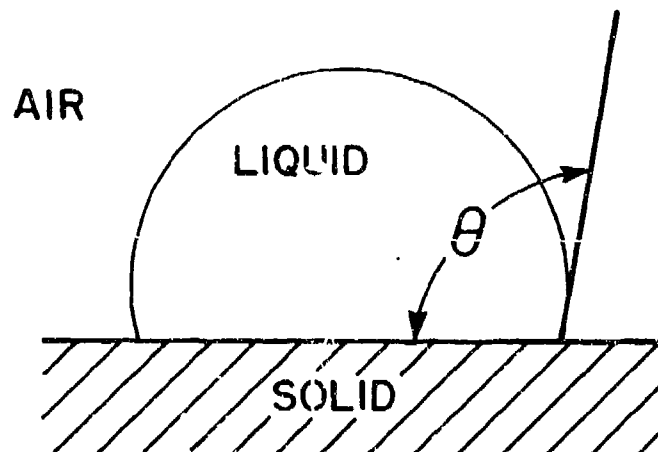
Schlosser in a recent paper (18) states that the special properties of fluorine result from its position in the periodic table. The nine protons in the nucleus of the element interact strongly with the same number of electrons, since all of them occupy inner shells. Thus, the van der Waals radius of fluorine ($r_F \sim 0.135$ nm) is contracted to such an extent that it closely resembles that of a hydrogen atom ($r_H \sim 0.110$ nm). Fluorine is the only element which can replace hydrogen without notable steric consequences.

Presumably, it is this strong interaction of the electrons of fluorine with the positively charged nucleus which is the cause of the low intermolecular forces and thus the low surface tensions found in fluorinated organic liquids. This same property results in the low melting points of fluorinated organic solids. In fluorine-containing polymeric substances, low intermolecular forces at the air/solid interface can give rise to surfaces with extremely low free energy. As a result, fluorine-containing polymers can be made which are difficult to wet with organic and aqueous liquids and it is this property which has led to our interest in these compounds. In addition, these surfaces tend to have nonadhesive character and low coefficients of friction.

(ii) ADSORBED MONOMOLECULAR FILMS CONTAINING FLUORINE

The unique non-wetting properties associated with a fluorochemical surface were discovered by W.A. Zisman at the U.S. Naval Research Laboratories in Washington (for an account of Zisman's work to 1964 see reference 17). This was accomplished by covering a polished solid surface such as platinum or stainless steel with a condensed monomolecular adsorbed film. For example, a monomolecular film of perfluorooctanoic acid ($\text{CF}_3(\text{CF}_2)_6\text{COOH}$) can be prepared by physical adsorption on platinum from a solution in an organic solvent (19). The carboxyl groups are then oriented at the platinum surface while the perfluorinated carbon chains stick out from the surface (19). From the study of many such surfaces, Zisman and co-workers were able to connect several structural features with wettability. Before this topic can be discussed further, the concepts of contact angle (θ) and the critical surface tension of wetting or spreading (γ_c) must be introduced. These concepts are essentially methods of measuring the liquid repellency of a surface or treated surface.

Figure 1. Contact Angle (θ) for a Pure Liquid on a Solid Surface



The contact angle θ , originally discussed by Young in 1805 (20), is illustrated in Figure 1. When $\theta = 0^\circ$, the liquid wets the solid completely and spreads freely over the surface. The greater the value of θ , the less tendency a liquid has to spread and thus the contact angle is a useful inverse measure of wettability. Experiments have revealed that every liquid wets every solid to some extent and thus $\theta \neq 180^\circ$. Fox and Zisman (14) noted that a linear relationship exists between cosine θ and surface tension for a homologous series of liquid n-alkanes on a treated surface. A plot of cosine θ versus the surface tension was extrapolated to $\cos \theta = 1$ (or zero contact angle) and this extrapolated value was defined as the critical surface tension of wetting or spreading, γ_c . Thus, liquids with surface tensions below the γ_c of the fluorinated substance will wet and spread freely on the solid, whereas liquids with surface tensions above γ_c will form discrete drops with contact angles greater than zero.

In their study of adsorbed monomolecular films, Zisman and co-workers studied the effect on γ_c of several important structural features. Each of the following will be discussed in turn: (i) progressively increasing the length of the perfluoroalkyl chain, (ii) the effect of a terminal CF_3 group at the end of a long hydrocarbon chain, and (iii) progressive fluorination along heptadecanoic acid ($\text{CH}_3(\text{CH}_2)_{15}\text{COOH}$) as compared with fully fluorinated heptadecanoic acid.

Monomolecular films of $\text{CF}_3(\text{CF}_2)_n\text{COOH}$ where $n = 2, 3, 4, 6, 8$ and 10 were adsorbed on platinum and their wetting properties were characterized (19). As shown in Section A of Table II, values of γ_c decreased from 9.2 to 5.6 dynes/cm as the values of n increased from 2 to 10. The value of $\gamma_c = 5.6$ for perfluorolauric acid ($n = 10$) is the lowest value found to date for any surface. Zisman and co-workers attribute these low γ_c values to the presence of a molecular orientation resulting in an exposed plane rich in perfluoromethyl groups. That is, the perfluorocarbon chains orient themselves so that a very high ratio of exposed CF_3 to CF_2 groups is obtained in the surface. An electron diffraction examination was consistent with this interpretation. The importance of the terminal CF_3 group can be appreciated by noting that a similar fluorinated acid ($n = 10$) terminated by CF_2H instead of CF_3 gave a γ_c value of 15 dynes/cm, which is more than twice the value of the CF_3 terminated acid (21).

The above results raised the interesting possibility that a compound such as trifluorostearic acid ($\text{CF}_3(\text{CH}_2)_{16}\text{COOH}$) bearing a terminal trifluoromethyl group should combine the desirable properties of a fluorine-rich surface and the enhanced molecular close-packing resulting from the van der Waals forces operative between adjacent hydrocarbon chains. This was not found to be the case. Shafrin and Zisman (15) showed that, although trifluorostearic acid was wet slightly less than stearic acid by n-alkanes ($\gamma_c = 18.4$ and 21.0 respectively), liquids able to form hydrogen bonds with the fluorine atoms of the film wet the trifluorostearic acid surface more. In comparison, although wetting data for the fully fluorinated stearic acid are not available, γ_c would be less than 6 dynes/cm (15).

It was shown by electron diffraction that although the stearic acid molecules were oriented almost wholly at 90° to the plane of the adsorbing surface, the films of trifluorostearic acid were less densely packed and

Table II. Values of γ_c For Various Substances^a

<u>Entry #</u>	<u>Compound</u>	<u>γ_c</u>	<u>Reference</u>
<u>A. γ_c For Perfluorinated Adsorbed Monolayers of Alkanoic Acids</u>			
1	CF ₃ (CF ₂) ₂ COOH	9.2	19
2	CF ₃ (CF ₂) ₃ COOH	9.0	19
3	CF ₃ (CF ₂) ₄ COOH	8.6	19
4	CF ₃ (CF ₂) ₆ COOH	7.9	19
5	CF ₃ (CF ₂) ₈ COOH	6.1	19
6	CF ₃ (CF ₂) ₁₀ COOH	5.6	19
<u>B. γ_c For Progressively Fluorinated Adsorbed Monolayers of Alkanoic Acids</u>			
7	CH ₃ (CH ₂) ₁₆ COOH	21.0	15
8	CF ₃ (CH ₂) ₁₆ COOH	18.4	15
9	CF ₃ CF ₂ (CH ₂) ₁₆ COOH	16.0	21
10	CF ₃ (CF ₂) ₂ (CH ₂) ₁₆ COOH	16.4	21
11	CF ₃ (CF ₂) ₄ (CH ₂) ₁₆ COOH	11.4	21
12	CF ₃ (CF ₂) ₆ (CH ₂) ₁₆ COOH	8.0	21
<u>C. γ_c For Smooth Polymer Surfaces</u>			
13	[CH ₂ -CH ₂] _n	31	26
14	[CH ₂ -CH(CF ₃)] _n	21.5	25
15	[CH ₂ -CH(CF ₂ CF ₃)] _n	16.3	25
16	[CH ₂ -CH(CF ₂ CF ₂ CF ₃)] _n	15.5	25
17	[CF ₂ -CF ₂] _n	18.5	14
18	[CF ₂ -CF(CF ₃)] _n	17	27
19	[CF ₂ -CF(n-C ₅ F ₁₁)] _n	14.1	25
20	[CH(COOCH ₂ (CF ₂) ₂ CF ₃)-CH ₂] _n	15.2	24
21	[CH(COOCH ₂ (CF ₂) ₆ CF ₃)-CH ₂] _n	10.4	24
22	[CH(COOCH(CF ₃) ₂)-CH ₂] _n	14.1	24
23	[CH(COO(CH ₂) ₂ OCF(CF ₃) ₂)-CH ₂] _n	13.5	24
24	[CH(COO(CH ₂) ₅ OCF(CF ₃) ₂)-CH ₂] _n	17.7	24

^a Units of γ_c are dynes/cm.

individual molecules were oriented at angles varying from 70° to 90°. Since the increase in steric hindrance caused by substituting the hydrogens by fluorine would be slight, the looseness in packing would most likely be caused by the dipole moment of 2.3 D associated with the presence of the CF₃ group in aliphatic compounds. Thus, this large dipole located in the outermost surface of the monolayer not only decreases the packing but creates an attractive field of force on the molecules of liquids and offsets or nullifies the advantages initially expected to result from the replacement of methyl by trifluoromethyl groups.

In a later paper (22), Shafrin and Zisman showed that this dipole had to be buried well below the surface before its effect was totally removed. Table II (section B) showed that the values of γ_C for CF₃(CF₂)_n(CH₂)₁₆COOH varied from $\gamma_C = 18.4$ to 8.0 for n = 0 to 6. In comparing the acids in section B of Table II with those in section A having the same perfluoroalkyl chain length, it is seen that the values of γ_C for the shorter perfluoro-segments are quite different while for the longer perfluoroheptyl substituent nearly identical values of γ_C are obtained (γ_C for CF₃(CF₂)₆COOH is 7.9 while that for CF₃(CF₂)₆(CH₂)₁₆COOH is 8.0). Thus, the dipole has been sufficiently removed from the external surface to have no influence on the adhesion of the liquid. Moreover, the presence of the 16-carbon hydrocarbon chain in the partially fluorinated acid has no effect on the wetting properties and, therefore, no effect on the closeness of packing of the terminal perfluoroheptyl moieties.

(111) SMOOTH, SOLID FLUOROPOLYMER SURFACES

The adsorbed molecular films described above are ideal cases in which it is possible for the fluorinated chains to pack very closely together to form surfaces rich in CF₃ groups. In polymers, the packing of fluoroalkyl groups is influenced by the orientation of the polymer backbone and the fact that the sites are fixed. Thus for the acrylates, fluoroalkyl groups can only be attached to alternate carbons. Table II (section C) lists several γ_C values for polymer surfaces. It is known that roughness increases the wettability and the results are for polymer films to which pressure and temperatures have been applied (300 lbs/inch² for 3h at 150°C (14)). Alternatively the polymer is applied by immersing glass slides in a coating solution, withdrawing them slowly, and heating the slide for a time (24,25).

Entry 13 in Table II shows that polyethylene has a γ_C of 31 dynes/cm. Replacement of one hydrogen by -CF₃, -CF₂CF₃ and -CF₂CF₂CF₃ (entries 14-16) reduces γ_C progressively to 21.5, 16.3 and 15.5 respectively. Replacement of hydrogens along the polymer backbone by fluorines also reduces γ_C . For example, polyethylene has a γ_C of 31 (entry 13) while teflon (entry 17) has a γ_C of 18.5. Replacement of a fluorine in Teflon by -CF₃ gave a γ_C of 17 (entry 18) and by -(CF₂)₄CF₃ gave 14.1 (entry 19). Entries 20-24 are acrylates having the general structure {CH(COOR_f)-CH₂}_n.

It is noteworthy that the acrylate having R_f = -CH₂(CF₂)₂CF₃ (entry 20) has nearly the same γ_C as the polyethylene polymer also bearing three fluorinated carbons (entry 16). When the number of fluorinated carbons in the acrylates is increased from 3 (entry 20) to 7 (entry 21) a drop in γ_C occurs from 15.2 to 10.4 dynes/cm. The last three acrylates all carry the perfluoroisopropoxy group. It is of interest to note that entry 22 carrying

the branched isopropoxy group has a slightly lower value of γ_C (14.1) than entry 20 having a straight chain fluorinated propyl group. However, the extra unfluorinated CH_2 in entry 20 most likely accounts for this small difference. Also, the isopropoxy group is attached directly to the acid function and would be a good leaving group (28). The more practical polymers having two and five intervening CH_2 's (entries 23 and 24) have γ_C 's which are greater (15.5 and 17.7 respectively) than that of the straight chain perfluoropropyl isomer (entry 20; $\gamma_C = 15.2$). Finally, as noted by Pittman (29), if the perfluorinated absorbed monolayers (entry 1 ($\gamma_C = 9.2$) and entry 4 ($\gamma_C = 7.9$)) are compared with the acrylates bearing the same perfluorinated groups (entry 20 ($\gamma_C = 15.2$) and entry 21 ($\gamma_C = 10.4$)), it is readily seen that the covalent attachment of the perfluorinated group to alternate carbon atoms along the polymer backbone hinders the ease of chain allineation.

(iv) FLUOROPOLYMERS AS FABRIC FINISHES

Textile fibers and fabrics do not present the smooth surfaces referred to above and even less the ideal surfaces used by Zisman in his monomolecular films. In fact, all of the smooth polymer films in Table II (section c) having γ_C 's as low as 10.4 dynes/cm would be wet by liquids having surface tensions of 20 dynes/cm or greater when these are applied as finishes to fabrics. For the rough surfaces of fabrics, a practical oil repellency test (AATCC 118-1966T) was developed (30). In the test, drops of standard hydrocarbon liquids of decreasing surface tension (see Table III) are placed across the surface of the fabric. The oil repellency rating of the fabric is the number of the liquid of the lowest surface tension which fails to wet and wick into the fabric. Adequate petrol repellency and anti-wicking properties develop at an oil repellency rating of approximately 6 (31).

In the mid 1950's, the phenomena discovered by Zisman for fluorinated materials began to be exploited in the treatment of textiles. First a chromium complex of perfluorooctanoic acid and then a vulcanizable rubber based upon 1,1-dihydroheptafluorobutyl acrylate were introduced on a commercial scale (32). In 1960, DeMarco and associates (1) further assured the commercial acceptance of fluorochemical finishes by showing that significant synergistic effects could be obtained from the addition of certain cheaper water repellents to a fluorochemical. These could not be predicted from the additive effect of the separate components. The structure of the fluorochemical used was not reported in their paper.

Grajeck and Petersen (33) showed conclusively for a series of poly-1,1-dihydroperfluoroacrylates $[\text{CH}(\text{COOCH}_2\text{R}_f)\text{-CH}_2]_n$ that, although the surface tensions of liquids wetting the fabric finishes were much higher (about 3 times) than those found in monomolecular films, similar effects were obtained on lengthening the fluoroalkyl chain (see Table IV). Thus, for the fluorinated group $-\text{C}_9\text{F}_{19}$ attached to the acrylate finish, a liquid with a surface tension of about 22 dynes/cm would wet the fabric while for a monomolecular layer containing the same group (entry 5 in Table II) a γ_C of 6.1 was obtained. These workers showed that nearly all of the potential

Table III. Physical Properties of Standard Test Liquids

Test Liquid	AATCC Number- Oil-Repellency Rating ¹	Surface Tension (30) (Dynes/cm at 25°C)
Nujol	1	31.45
65/35 Nujol/n-Hexadecane	2	29.6
n-Hexadecane	3	27.3
n-Tetradecane	4	26.35
n-Dodecane	5	24.7
n-Decane	6	23.5
n-Octane	7	21.4
n-Heptane	8	19.75

¹ At DREO half grades are assigned for experimental purposes. Thus a rating of 4/5 would be for a liquid consisting of a 50:50 volume % mixture of 4 and 5.

Table IV. Repellency on Cotton for a Series of Polyacrylates
R_fCH₂O-Acrylates (33)

R _f ¹	Oil Repellency ²	Spray Rating ³
-CF ₃	0	50
-C ₂ F ₅	1.5-2	70
-C ₃ F ₇	4.5-5	70
-C ₅ F ₁₁	5.5-6	70
-C ₇ F ₁₅	6.5-7	70
-C ₉ F ₁₉	7-7.5	80

¹ Straight-chain fluoroalkyl substituents

² Oil repellency was originally reported on the earlier 3M oil repellency scale of 50-150. These levels are converted to the approximate standard AATCC rating by extrapolation of the known surface tensions of the test liquids involved (30, 31, 33).

³ AATCC spray test (see Table V)

Table V. Water-Repellency Spray Test Ratings

Rating	Description
100	No sticking or wetting of upper surface
90	Slight random sticking or wetting of upper surface
80	Wetting of upper surface at spray points
70	Partial wetting of whole of upper surface
50	Complete wetting of whole of upper surface
0	Complete wetting of whole upper and lower surfaces.

oil and water repellencies were developed at concentrations of 1% solids on the fabric but that the durability of these finishes to laundering and dry cleaning improved directly with increased concentration (levels of 2% are desirable). The use of selected water repellents as co-applicants to the fluoroalkyl acrylates to effect a synergistic improvement in both oil repellency and spray ratings, especially at lower bath concentrations was also demonstrated (33).

The commercial utility of the fluoroalkyl-substituted acrylate and methacrylate polymers was further demonstrated by a series of patents issued to Dupont in 1966 (34). Values of 7 (oil repellency) and 100 (water repellency) were obtained by finishes containing 25% or less of fluoroalkyl substituted methacrylate $[C(CH_3)(COOR_f)-CH_2]_n$ polymer while the remainder consisted of an acrylate or methacrylate polymer containing no fluorine. The fluorinated substituents (R_f) required to give these high repellencies were $-(CF_2)_6CF_3$ and $-(CF_2)_8CF_3$. These patents also state that the results obtained with the mixture of fluorinated and non-fluorinated polymers are superior to those obtained with the fluorinated polymers themselves. The molecular weight of both the fluorinated and non-fluorinated polymers was not a controlling factor as useful repellents were obtained over a wide range of molecular weights.

A good explanation of the synergism described above has not yet been given. It does not occur when the fluoroalkyl methacrylates are mixed with the common methylhydrogen- or dimethylsiloxane water repellents. In fact, just the opposite occurs. Even traces of these siloxanes cause an appreciable reduction in oil repellency (3,5,31,33,35).

The question of whether branched fluoroalkyl substituents achieve greater liquid-repellent properties than their straight-chain counterparts appears to be somewhat controversial. On the other hand, Pittman and co-workers in several patents (6,7,36) state that the branched perfluoroisopropyl substituent, $(CF_3)_2CF-$, yields a degree of oil repellency equivalent to 6 or 7 fluorinated carbons in a straight chain. However, in a recent publication (3), Lichstein states that it would appear that the main purpose of the work with branched chain fluorocarbons is to avoid infringements on patents which are based on straight-chain fluorocarbons. He expresses surprise at Pittman's claims for the perfluoroisopropoxy group. In one respect the idea of branching is a good one. As indicated by Zisman's work, the best liquid-repellent properties are obtained by a surface of closely packed trifluoromethyl groups. Thus, $-CF(CF_3)_2$ which can theoretically have two CF_3 groups per substituent in the surface would effect a much better liquid repellency. To achieve such a surface density of CF_3 groups, two conditions need to be met. First, the polymer backbone structure and the arrangement of the F and two CF_3 groups must permit efficient packing and second, that the dipole created by the three fluorine-containing groups does not cause hindrance to packing or attraction to liquids.

Several papers have addressed the question of branching. For monomolecular films it has been found that branching of a perfluoroalkyl chain disrupts close packing and hence causes lower values of γ_C (3,23). Thus, $(CF_3)_2CF(CF_2)_{11}COOH$ has a γ_C of 13.3 dynes/cm which is more than twice that of

the straight-chain acid. Also the acid $(CF_3)_2CFCF_2COOH$ results in a γ_C of 15.2 while the corresponding straight-chain acid has a γ_C of 9.0.

It has been shown by Pittman and co-workers (37,38) that poly(perfluoro-t-butyl) acrylate has an oil repellency of 4. The value for this polymer, which has three CF_3 groups per substituent $(-C(CF_3)_3)$, is actually lower than the value of 5 expected for the corresponding straight-chain polymer (see Table IV, $R_f = -C_4F_9$). Pittman (37) concludes that the constraints upon the orientation of the side chains imposed by the polymer backbone are severe enough to prevent efficient packing of the fluoroalkyl groups at the interface. Thus, the use of different polymer backbones may prove to be beneficial. A recent publication by 3M Co. (39) patents several compounds containing the perfluoro-t-alkyl group having the structure $[(R_f)(R_f)(CF_3)C-]$ where R_f is a perfluoroalkyl radical of less than 10 carbon atoms. A report on the liquid-repellent properties of these compounds may thus be forthcoming.

The heptafluoroisopropoxy group has been of great interest in the branching question. Pittman and co-workers (6,7,36) state that this group can give an oil repellency equivalent to a straight chain substituent having about twice the number of fluorines. Indeed the acrylate, $\{((CF_3)_2FCOOC)CH-CH_2\}_n$ has a γ_C of 14.1 which is somewhat better than the γ_C of 15.2 reported for the smooth polymer film of the straight chain substituent $\{(CF_3CF_2CF_2CH_2OOC)CH-CH_2\}_n$ (24). However, this could be due to the difference in hydrogen content since the branched methacrylate, $\{((CF_3)_2CFOOC)(CH_3)C-CH_2\}_n$, which has the same hydrogen content as the preceding straight chain acrylate, has a γ_C value of 15.0, nearly identical to that of its straight-chain isomer (24).

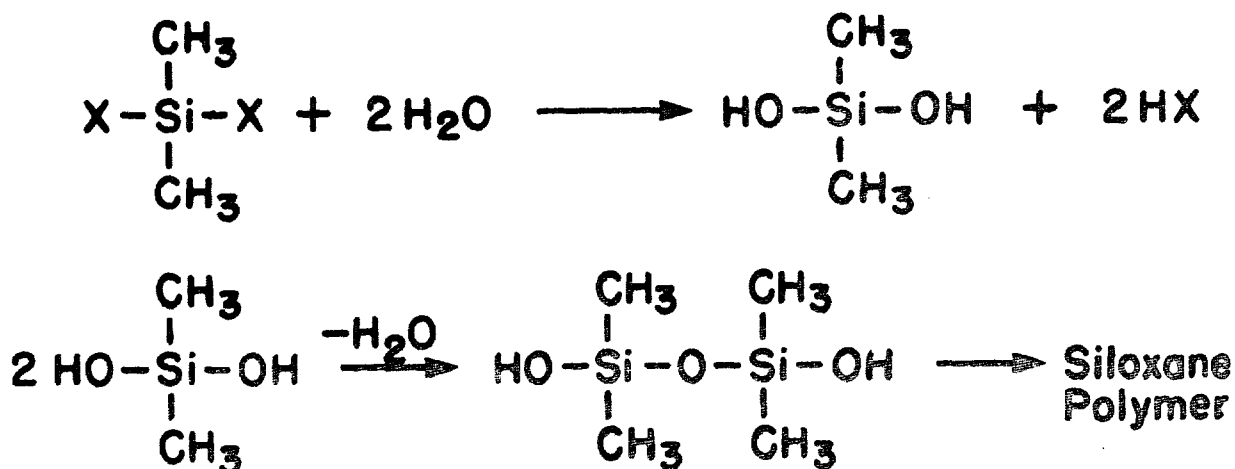
It has been shown that oil repellencies in the region of 4-5 can be obtained with polyheptafluoroisopropyl acrylate (28,40). However, repellencies in this same region can be obtained with the acrylate containing the straight-chain $CF_3CF_2CF_2CH_2O-$ substituent (see Table IV). Thus, the above arguments appear to suggest that there is very little, if any, advantage in the use of branched- over straight-chain acrylates and methacrylates. However, it may be that the apparent theoretical advantage of the greater number of $-CF_3$ groups in the branched-chain substituents could be achieved in polymers with different backbones.

C. NON-FLUORINATED SILOXANES

Organosilanes are extremely important industrial compounds and are useful in many varied processes. For many years, the silicones have been used as water repellents, antifoaming agents, and polish ingredients. A good review of these uses up to 1959 has been given by K.L. Bass (2). A more recent paper (41) shows that the organosilanes have established their place in many high technology uses. They are used as bonded phases for gas and liquid chromatography, in thermoset composites, in solid-state synthesis, and so on. However, our interest in the organosilanes is in their use as liquid repellents and as a backbone on which to place our fluorinated substituents.

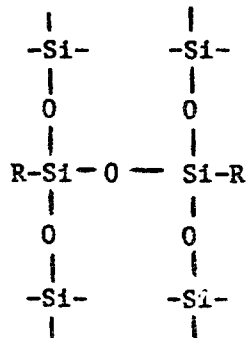
Siloxanes are polymeric materials in which the basic polymer chain is composed of alternate silicon and oxygen atoms. The most common siloxanes which are used as water repellents are polydimethylsiloxane and polymethylhydrogensiloxane. Siloxanes for textiles are for the most part mixtures of both (3). The hydrogens can condense with the functional groups on the textile surface. Metal soap catalysts or titanium compounds are used to fix the finish.

The formation of the siloxane polymer chain is shown below for polydimethylsiloxane (X is any hydrolyzable group such as halogen or alkoxy; R = CH₃),



In the first step, the hydrolyzable groups react with water to form silanols. Two silanols can then condense to form an $-\text{Si}-\text{O}-\text{Si}-$ unit with the loss of water. The silanol end groups can then condense further and eventually a polymer of high molecular weight is obtained. This is the method by which by both fluorinated and non-fluorinated siloxane polymers are formed. Generally a small amount of catalyst, either basic or acidic, is used to speed up the reaction (42).

The siloxane shown above is an example of a linear polymer. When three hydrolyzable groups are present on the silane, a network polymer is formed (see below). In the work to be described in the second report on this topic, the effectiveness of linear and network siloxanes containing fluorinated substituents will be compared.



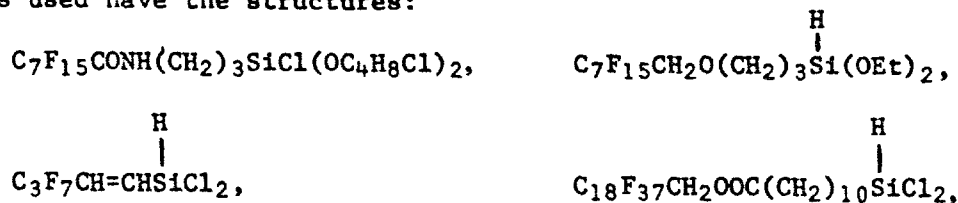
The mode of action of a repellent silicone finish is produced by the methyl groups facing away from the surface of the fabric to which the backbone of the polymer is attached by covalent bonds (reaction of terminal silanols with functional groups on the fabric), hydrogen bonding, and dipole-dipole interactions (43). Much of the work on the surface active properties of polyorganosiloxanes was carried out in the 1940's (44). The first commercial compositions in which silicones were applied as water repellents became available in the 1950's (2,45,46). Silicone water repellents display a high degree of durability of washing and drycleaning (47). Although excellent and durable water repellency could be obtained with these silicones, they have no resistance to oils. In order to develop this desirable property, fluorinated substituents with lower critical surface tensions than methyl must be tacked onto the siloxane backbone.

D. FLUOROALKYL-SUBSTITUTED SILOXANES AS AQUEOUS AND ORGANIC LIQUID REPELLENTS

The available literature on fluoroalkyl siloxanes is mostly to be found in patents. This is not surprising since water and oil repellency and the resultant anti-staining properties are very useful commercial properties. However, with patents on commercially competitive topics, it can be extremely difficult to get at the core information or even to be able to follow exactly what was done (see the comments on this topic in references 10 and 48). Detail is frequently lacking and examples can be the inventors' teaching of the invention and not necessarily actual experiments.

The claims made in the patent literature for the fluoroalkyl siloxanes were certainly worth our attention. However, the results obtained from one patent process to another could not be compared because non-standard test methods were often used, in some cases key values were not given, and fluorinated siloxanes with perhaps more desirable structural features were not tested. It is our intention in this section to review the more important work in this area and, in the next two sections, to indicate how the most applicable work will be evaluated and extended. The usual procedure for the patents in this area is to put down a general formula claiming hundreds of compounds and then to discuss the few on which the work was done. Only compounds of interest which were actually used in the patents will be mentioned here.

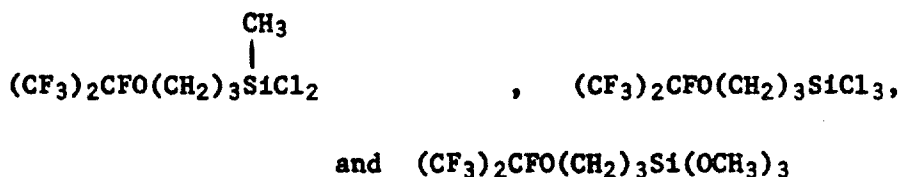
The pioneering patents on silanes containing fluoroalkyl substituents were those granted to Holbrook and Steward (4) in 1961 and 1962. The monomers used have the structures:



and $(\text{CF}_3)_2\text{CHCH}_2\text{SiH}_3$

These monomers, which are of quite varied structure, were polymerized with 0.01 N hydrochloric acid (Si-H bonds cleave in base) and the resultant polymers were applied to wool fabric using ether as solvent. Unfortunately, oil repellency was tested by measuring the time required for a drop of commercial lubricating oil to soak into the fabric. Since this is not a standard test, there is no way that the oil repellency obtained can be compared with that reported in other patents. Also no numerical data were given for water repellency. Lewis in 1974 (31) states that these patents have not been exploited commercially.

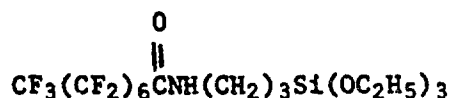
In a series of publications (5,6,7a) beginning in 1969, Pittman and Wasley patented the synthesis and various uses of a number of fluorinated isopropoxy siloxanes. The best results were obtained with the structures:



Water repellency values obtained with the polymers of these compounds were as high as 90 and 100. The oil repellency ratings, however, were only mid range on the 3M scale (values of 80 and 90, which correspond to approximately 4-4.5 on the standard scale). The methods of polymerization and application to fabric for these monomers are somewhat complex. This may be the reason for the lack of commercial exploitation of these finishes (at least up to 1974 (31)). The preparation of the polymer finish from the above trichlorosilane monomer involved a stirring period with water, several washes with water, a cross-linking step at 140-150°C for several hours (necessary to achieve maximum oil repellency (5)), and final dissolution in a fluorinated solvent (trichlorotrifluorosilane).

The liquid-repellent properties of the treated fabrics are durable; they are retained despite laundering and drycleaning. The mid-range values of the oil repellencies obtained with these compounds are not sufficient for military purposes where ratings of 6 are preferred. An important point concerning the trialkoxy silane derivatives (see the last structure above) are that they do not release hydrohalic acid when contacted with substances containing active hydrogen (as in -OH, -NH₂, and like groups). Thus, in applications to substrates such as fabrics, the use of alkoxides avoids the possibility of damage. It is for this reason that the monomers used in the preparation of finishes in this project are either the methoxy or the ethoxy silane derivatives. In 1974 (7b) and 1977 (36) patents, Pittman and Wasley employed the above-mentioned fluorochemical substituents and others as copolymers with hydrophilic monomers to give finishes which impart the commercially desirable properties of soil repellency and soil releasability. These finishes are useful in that they have some oil repellency and, when a stain is forced upon a treated fabric, it can be wetted and washed. Water repellency, of course, is greatly reduced.

An interesting patent was issued to Nalco Chemical Co. in 1972 (8), in which the fluoroamidoalkyl silane shown below was utilized to obtain good oil and water repellency:



This is the patent which increased our interest in the fluoroalkyl siloxanes since the values given (oil repellency of 6 and water repellency of 100) are very close to those required for military finishes. The experimental details provided, however, are very vague and the repellency values given are for wool fabric only.

THE OBJECTIVES OF THE STUDY AND THE OVERALL APPROACH

The main objective of the study is to evaluate fluorinated alkyl polysiloxanes as liquid repellent finishes. The approach taken was to synthesize a series of monomers with a variety of structures (including the best ones reported in the literature), to ascertain the best method of polymerization of the monomers, and to evaluate them in terms of the oil and water repellency which they impart to cotton and nylon/cotton. The structures of the selected monomers are shown in Table I. The numbering system assigned will be used throughout this report. Two types of polymers can be obtained from the monomers in Table I. Network polymers will be obtained from 1, 3, 5, 7 and 9 (since three hydrolyzable groups are present on the silane) while 2, 4, 6 and 8 will yield linear polymers (only two hydrolyzable groups on the silane). From these comparisons a clear indication concerning which type of polymer is better should be obtained.

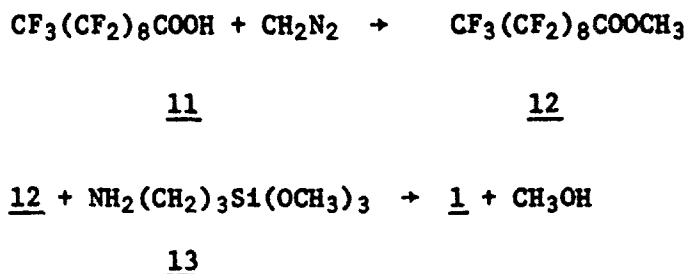
There are four perfluoroalkyl substituents of different structures present in Table I. There are two straight-chain substituents of varying length ($\text{CF}_3(\text{CF}_2)_8-$, 1 and 2; and $\text{CF}_3(\text{CF}_2)_6-$, 3, 4, 5 and 6) and two branched chain substituents ($(\text{CF}_3)_2\text{CF}-$, 7 and 8; $(\text{CF}_3)_3\text{C}-$, 9 and 10). Also two different functional groups are present (1-4 are amides while 5-10 are ethers).

Of crucial importance, of course, are the liquid-repellent properties of the homopolymers, but since the cost of these fluorochemicals would be high, a study of their copolymerization with much cheaper non-fluorinated silanes would also be of great value. Other desirable data to obtain would be: washing and wearing characteristics; the level of add-on which would be necessary to achieve fire resistance (if any); the level of phosphate resistance; and the comparison of the best results with those of commercially available formulations. The synthetic aspects of the monomers will be considered in this report (see the next section and the experimental).

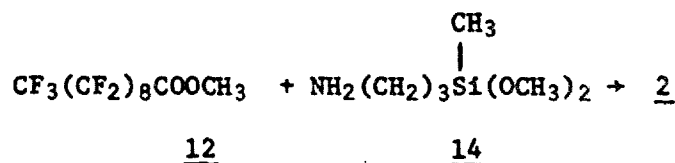
THE SYNTHESIS OF THE FLUORINATED SILANE MONOMERS

There are several limitations on the introduction of a perfluorinated alkyl substituent into a silane monomer (41,49). Silicon is less electronegative than carbon. Consequently, introduction of electronegative substituents on the alkyl chain close to silicon increases the reactivity of the Si-C bond immensely. For example, aqueous base readily cleaves the C-Si bond of polyfluoroalkyl silicon compounds which contain fluorine on carbons α or β to silicon (49). Also these compounds have relatively low thermal stability. For this reason, all of the compounds in Table I have a propyl group between the silicon atom and the part of the monomer containing the electronegative fluoroalkyl substituent.

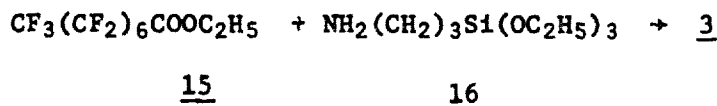
The amide 1 was prepared in two steps. The commercially available perfluorodecanoic acid 11 was converted to the methyl ester 12 with diazomethane and the ester was converted to 1 by treatment with γ -aminopropyltrimethoxysilane 13.



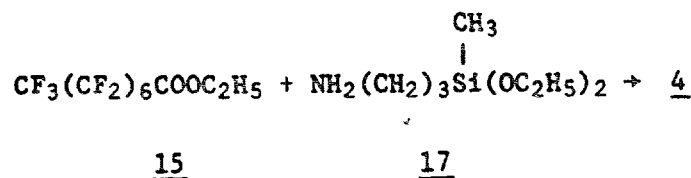
The triethoxy amine cannot be used in this reaction since the methanol formed would exchange readily with the silane ethoxy substituents to give a mixed methoxy-ethoxy silane. The corresponding dimethoxymethyl silane 2 was obtained by treating the methyl ester 12 with γ -aminopropyl dimethoxymethylsilane 14:



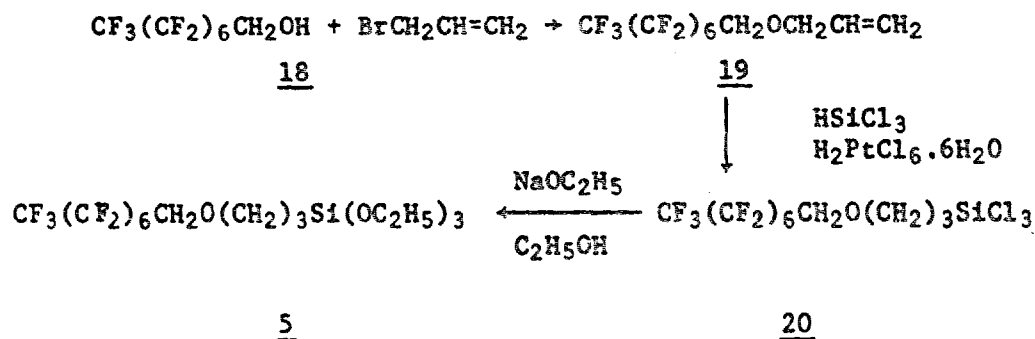
The amide 3 was obtained by reacting the commercially available ethyl ester of perfluorooctanoate 15 with γ -aminopropyltriethoxysilane 16 as described in reference 8.



The use of the diethoxymethylsilane derivative 17 in the above reaction yielded the amide 4.



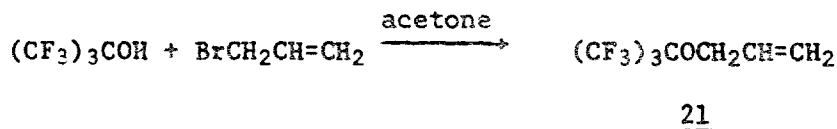
For synthesis of the ether 5, the requisite alcohol 18 was first treated with alkyl bromide to form the olefin 19. Reaction of the latter with trichlorosilane in the presence of chloroplatinic acid gave the trichlorosilane 20, which provided the monomer 5 on treatment with a 10% excess of sodium ethoxide in absolute ethanol.



The use of a slight excess of sodium ethoxide is critical in the reaction. A greater excess decreases the yield of product and the use of only absolute ethanol gives mainly dimers and trimers (The hydrochloric acid produced in the reaction converts some ethanol into ethyl chloride and water. The water causes the condensation of monomer units). When methyldichlorosilane is used with the olefin 19 and the resultant product is treated with ethanol/sodium ethoxide solution, the monomer 6 is obtained.

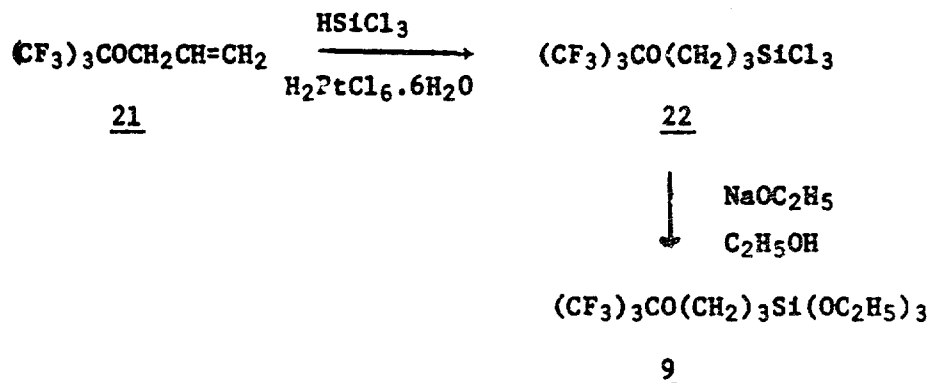
The trichloro- and dichloromethylsilane precursors of 7 and 8 were available commercially and these were converted to the ethoxysilane derivatives by the use of ethanol/sodium ethoxide solution.

The monomer 9 proved to be the most difficult compound to synthesize. The first step in the synthesis was the reaction of perfluorinated t-butyl alcohol with allyl bromide:



The reaction is conducted in acetone by heating the solution under reflux. The low boiling point of the perfluorinated alcohol (44-5°) in comparison with those of the other components of the solution (70° for allyl bromide and 56° for acetone) complicates the synthesis if a water condenser is used since the

most volatile component tends to escape before it has completely reacted. Also the boiling points of the product 21 and allyl bromide are so close together that they cannot be separated by careful fractionation. It is therefore essential to drive the reaction to completion to facilitate the purification of the product. This was effected by using a slight excess of the fluorinated alcohol together with a dry-ice condenser to prevent its slow escape. By following the progress of the reaction with nmr spectroscopy it was found that all the allyl bromide had reacted after 5 days. The product 21 was also difficult to separate from the acetone by distillation. However, this problem was circumvented by adding the reaction mixture to toluene, extracting the acetone with water and distilling 21 from the toluene solution. Reaction of 21 with trichlorosilane in the presence of chloroplatinic acid gave the trichlorosilyl derivative 22, which, following isolation and reaction with sodium ethoxide in absolute ethanol, furnished the monomer 9.



The olefin 21 on reaction with dichloromethylsilane, followed by sodium ethoxide in absolute ethanol gave the monomer 10.

For the copolymerization experiments with non-fluorinated monomers, the tetraethoxy- and methyltriethoxysilanes were obtained commercially. The monomers hexyl- and dodecyltrichlorosilanes were obtained commercially and converted to the triethoxy derivatives. Since monomers of comparable reactivity were required in the copolymerization experiments and all of the non-fluorinated monomers were ethoxy derivatives, it was necessary to synthesize the ethoxy derivatives of 1 and 2. This was done by using the corresponding γ -aminopropylethoxysilane in the reaction with methyl perfluorodecanoate and then refluxing the product in dry ethanol to exchange those methoxy substituents which had replaced ethoxyl in the condensation reaction.

EXPERIMENTAL

Starting materials (obtained mainly from PCR, Inc. and Silar Laboratories, Inc.) were generally used as received. However, further purification was occasionally necessary. All temperatures are in degrees centigrade. A Varian T-60 Nuclear Magnetic Resonance (nmr) Spectrometer was used to record proton spectra. Unless otherwise stated spectra were obtained with deuterated chloroform solutions containing tetramethylsilane as an internal standard. All chemical shifts are reported in parts per million (ppm, δ scale) and the letters s, d, t, q, p, m and br were used to designate singlet, doublet, triplet, quartet, pentuplet, multiplet, and broad respectively. Fluorine nuclear magnetic resonance (fnmr) spectra were obtained with the same instrument using a fluorine probe. All chemical shifts are in ppm relative to external fluorotrichloromethane. Neat solutions were used unless otherwise stated and fine structures were determined on an expansion scale of 10 ppm. Infrared spectra were recorded on a Perkin Elmer Model 283 infrared Spectrophotometer. Values are given in cm^{-1} and chloroform was used as the solvent unless otherwise stated.

METHYL PERFLUORODECANOATE

Perfluorodecanoic acid (25.7 g, 0.0500 mol) was dissolved in anhydrous diethyl ether and to this stirred solution was added a diethyl ether solution of diazomethane (prepared as reported by Vogel (50)) until the yellow colour persisted. The solvent was removed in vacuo and the crude ester was distilled at 28 Torr. The clear colourless oil boiling at 98-101° was collected (23.6 g, 89%). Nmr 4.02 (sharp s, ester methyl); Ir (NaCl) 1793 (ester C = O); Fnmr (CDCl_3) 140.1(3F, t, CF_3), 101.9(2F, br s, CF_2), 98.5 and 97.5 (1.2F, two overlapping br s, CF_2 's), 93.7(2F, br s, CF_2).

3-PERFLUORODECYLAMIDOPROPYLTRIMETHOXYSILANE 1

The procedure used here is a modification of one reported by Nalco Chemical Company (8). 3-Aminopropyltrimethoxysilane (12.5 g, 0.0698 mol) was added dropwise from a pressure-equalizing dropping funnel to methyl perfluorodecanoate (36.0 g, 0.0682 mol). Slight evolution of heat occurred during the addition. The solution was heated at 70° for 3 h and the methanol was removed at reduced pressure. The remaining yellowish oil was distilled at 0.1

Torr and the liquid boiling at 125-129° was collected (43.2 g, 94%). The distillate solidified (mp 41-43°). Nmr 7.38 (1H, broad s, NH), 3.64 (9H, s, methoxyls), 3.49 (2H, q, overlap of one peak with methoxyl, CH₂ next to nitrogen), 1.80 (2H, p, central CH₂), 0.71 (2H, t, CH₂ next to silane) (J = 7-8 Hz for methylene couplings); fnmr (CDCl₃) 140.6 (3F, t, CF₃), 100.9 (2F, br s, CF₂), 98.9 and 98.1 (12F, two overlapping br s, CF₂'s), 94.3 (2F, br s, CF₂); ir 3439 (NH free), 3290 (NH bonded), 1721 (amide C = O), 1518 (CONH), 1240-1080 (several overlapping strong bands, OCH₃, CF, Si-O-C).

DIMETHOXYMETHYL-3-PERFLUORODECYLAMIDOPROPYLSILANE 2

3-Aminopropyldimethoxymethylsilane (8.0 g, 0.0471 mol) was treated with methyl perfluorodecanoate (25.0 g, 0.0474 mol) using the same procedure as detailed in the synthesis of 1. The product which had a bp of 122-125°/0.1 Torr, solidified (m.p. 36.5-38.5°) following distillation (29.0 g, 93%). Nmr 7.47 (1H, br s, NH), 3.56 (6H, s, methoxyls), 3.42 (2H, q, overlap of one peak with methoxyl, CH₂ next to nitrogen), 1.75 (2H, p, central propyl CH₂), 0.67 (2H, t, CH₂ next to silane), 0.14 (3H, s, silane methyl) (J = 7-8 Hz for all methylene couplings); fnmr (CHCl₃) 140.1 (3F, t, CF₃), 100.6 (2F, br s, CF₂), 98.6 and 98.0 (12F, two overlapping br s, CF₂'s), 94.3 (2F, br s, CF₂); ir 3439 (NH free), 3280 (NH bonded), 1721 (amide C = O), 1518 (CONH), 1242-1070 (several overlapping strong bands, OCH₃, CF, Si-O-C).

3-PERFLUOROOCYLA MIDOPROPYLTRIETHOXY SILANE 3

3-Aminopropyltriethoxysilane (25.0 g, 0.113 mol) was treated with ethyl perfluorooctanoate (50 g, 0.113 mol) using the same procedure as described for the synthesis of 1. The clear colourless viscous oil boiling at 126-128°/0.2 Torr was collected (61.6 g, 88%). Nmr 7.38 (1H, br s, NH), 3.89 (6H, q, CH₂'s of OC₂H₅), 3.45 (2H, q, CH₂ next to nitrogen), 1.77 (2H, p, central propyl CH₂), 1.25 (9H, t, methyls of OC₂H₅), 0.66 (2H, t, CH₂ next to silane); fnmr 139.0 (3F, t, CF₃), 100.2 (2F, br s, CF₂), 97.5 (8F, br s, CF₂'s), 93.2 (2F, br s, CF₂); ir 3440 (NH free), 3295 (NH bonded), 1719 (amide C = O), 1525 (CONH); n_D²⁵ 1.3687).

DIETHOXYMETHYL-3-PERFLUOROOCYLA MIDOPROPYLSILANE 4

3-Aminopropyldiethoxymethylsilane (8.65 g, 0.0453 mol) was treated with ethyl perfluorooctanoate (20.0 g, 0.0452 mol) using the same procedure as described for the synthesis of 1. The clear colourless oil boiling at 118-121°/0.2 Torr (21.0 g, 79%) was the required product. Nmr 7.38 (1H, br s,

NH), 3.84 (4H, q, CH₂'s of OC₂H₅), 3.44 (2H, q, CH₂ next to nitrogen), 1.74 (2H, p, central propyl CH₂), 1.24 (6H, t, methyls of OC₂H₅), 0.64 (2H, t, CH₂ next to silane), 0.14 (3H, s, silane methyl); τ 139.0 (3F, t, CF₃), 100.0 (2F, br s, CF₂), 97.2 (8F, br s, CF₂'s), 93.0 (2F, br s, CF₂); ν_{max} 3441 (NH free), 3325 (NH bonded), 1720 (amide C = O), 1524 (CONH); n_{D}^{25} 1.3684.

ALLYL-1,1-DIHYDROPERFLUOROCTYL ETHER 19

The method of Holbrook and Steward (4) was used. 1,1-Dihydroperfluorooctanol (28 g, 0.07 mol), allyl bromide (12.6 g, 0.0104 mol), and 19.2 g of anhydrous potassium carbonate were mixed with acetone (35 ml) and refluxed for 3.5 days. The mixture was filtered and the acetone and excess allyl bromide were removed on the rotary evaporator under reduced pressure. Distillation of the residue at 24 Torr gave a clear colourless oil (bp 80-83° (lit.(4) 177.8-178.1° (745 Torr)), 28.6 g, 93%). Nmr 5.93 (1H, m, CH), 5.30 (2H, m, olefinic CH₂), 3.93 (2H, t, CH₂ split by CF₂, J = 14.2 Hz), 4.14 (2H, d, CH₂ next to double bond, J = 5.5 Hz).

3-(1,1-DIHYDROPERFLUOROCTOXY)-PROPYLTRICHLOROSILANE 20

To a solution of allyl-1,1-dihydroperfluorooctyl ether (28.7 g, 0.0652 mol) and trichlorosilane (27.1 g, 0.200 mol) was added 0.4 ml of an isopropanol solution containing 73 mg of chloroplatinic acid per millilitre. The solution was refluxed overnight and the excess trichlorosilane was distilled off. The residual oil was distilled at 3 Torr and the colourless oil, bp 83-89° (25.4 g, 68%) was the required product (lit(3), 125°/7.5 Torr). Nmr (neat, external TMS) 3.82 (2H, t, CH₂ next to CF₂, J = 14 Hz), 3.55 (2H, t, propyl CH₂ next to oxygen, J = 6), 1.53 (4H, m, central propyl CH₂ and CH₂ next to silane).

3(1,1-DIHYDROPERFLUOROCTOXY)-PROPYLTRIETHOXSILANE 5

Sodium metal (3.36 g, 0.146 gram atom) was cut into several pieces and then added to absolute ethanol (125 ml). After the reaction was complete, the sodium ethoxide solution was cooled in ice and 3-(1,1-dihydroperfluorooctoxy)-propyltrichlorosilane 20 (25.4 g, 0.0441 mol) was added dropwise from a pressure-equalizing dropping funnel. The mixture was allowed to warm up to room temperature, then stirred for 2 h. The precipitated sodium chloride was removed by filtration using a sintered glass funnel, and the ethanol was removed on the rotary evaporator under reduced pressure. The residue was distilled at 0.2 Torr to give a colourless oil (bp 99-103°, 16.3 g, 61%). Nmr 3.88 (10H, q of the ethoxyl CH₂'s on top of a multiplet for

the CH₂'s on either side of the oxygen), 1.79 (2H, m, central propyl CH₂), 1.25 (9H, t, ethoxyl CH₃'s), 0.65 (2H, m, CH₂ next to silane); fnmr 139.1 (3F, t, CF₃), 100.1 (2F, br s, CF₂), 97.5 and 96.5 (8F, two br overlapping s, CF₂'s), 93.2 (2F, br s, CF₂); n_D^{25} 1.3533.

DICHLORO-3-(1,1-DIHYDROPERFLUOROCTOXY)-PROPYLMETHYLSILANE

To a solution of allyl-1,1-dihydroperfluorooctyl ether (17.9 g, 0.0407 mol) and dichloromethylsilane (10.0 g, 0.0870 mol) was added 0.19 ml of an isopropanol solution containing 73 mg of chloroplatinic acid per millilitre. The solution was heated under reflux overnight and the excess dichloromethylsilane was removed by distillation. The residue was distilled and the colourless oil boiling at 75-77°/0.05 Torr (17.0 g, 75%) was collected. Nmr 3.98 (2H, t, CH₂ next to CF₂, J = 14 Hz), 3.69 (2H, t, propyl CH₂ next to oxygen, J = 6 Hz), 1.86 (2H, m, central propyl CH₂), 1.22 (2H, m, CH₂ next to silane), 0.79 (3H, s, silane methyl).

DIETHOXY-3-(1,1-DIHYDROPERFLUOROCTOXY)-PROPYLMETHYLSILANE 6

The same procedure was used as for the synthesis of 5. Sodium (2.02 g, 0.0878 gram atom), absolute ethanol (100 ml), and dichloro-3-(1,1-dihydroperfluorooctoxy)-propylmethylsilane (22.2 g, 0.0400 mol) when reacted and worked up using this procedure gave 16.2 g (70%) of clear colourless oil, bp 86-89°/0.1 Torr. Nmr 3.81 (8H, q of the ethoxyl CH₂'s on top of a multiplet for the CH₂'s on either side of the oxygen), 1.74 (2H, m, central propyl CH₂), 1.23 (6H, t, ethoxyl CH₃'s), 0.65 (2H, m, CH₂ next to silane), 0.12 (3H, s, silane methyl); fnmr 139.2 (3F, t, CF₃), 99.9 (2F, s, CF₂) 97.4 and 96.2 (8F, two br overlapping s, CF₂'s), 93.1 (2F, br s, CF₂); n_D^{25} 1.3524.

3-PERFLUOROISOPROPOXYPROPYLTRIETHOXY-SILANE 7

Sodium (5.7 g, 0.248 gram atom), absolute ethanol (150 ml), and 3-perfluoroisopropoxypropyltrichlorosilane (25.7 g, 0.0712 mol) were reacted and worked up using the procedure described for the synthesis of 5. The product was a clear, colourless oil (bp 92-93°/30 Torr, 18.1 g, 65%). Nmr 3.89 (8H, q on top of a set of peaks, ethoxyl CH₂'s plus propyl CH₂ next to oxygen), 1.84 (2H, m, central propyl CH₂), 1.25 (9H, t, ethoxyl methyls), 0.68 (2H, m, CH₂ next to silane); fnmr 141.0 (6F, d, CF₃'s), 77.2 (1F, p, CF); n_D^{25} 1.3553.

DIETHOXYMETHYL-3-PERFLUOROISOPROPOXYPROPYLSILANE 8

Sodium (4.5 g, 0.196 gram atom), absolute ethanol (125 ml), and dichloromethyl-3-perfluoroisopropoxypropylsilane (30.5 g, 0.0895 mol) were reacted and worked up using the procedure described in the synthesis of 5. A clear colourless oil was obtained (bp 79-82°/30 Torr, 23.3 g, 72%). Nmr 3.83 (8H, q on top of a set of peaks, ethoxyl CH₂'s plus propyl CH₂ next to oxygen), 1.81 (2H, m, central propyl CH₂), 1.23 (9H, t, ethoxyl CH₃), 0.67 (2H, m, CH₂ next to silane), 0.13 (3H, s, silane CH₃); fmr 141.0 (6F, d, CF₃'s), 77.0 (1F, p, CF); n_D²⁵ 1.3545.

ALLYLPERFLUORO-t-BUTYL ETHER 21

Perfluoro-t-butyl alcohol (24.6 g, 0.104 mol) and allyl bromide (11.8 g, 0.0974 mol) were dissolved in acetone (55 ml). Potassium carbonate (26.8 g) was then added. After stirring at room temperature for 24 h an nmr spectrum on an aliquot of the reaction mixture showed only 20% reaction. A reflux condenser was attached and a dry ice condenser protected with a drying tube was added to it. This was necessary because of the volatility of the perfluoro-t-butyl alcohol. After five days of heating under reflux, the reaction was complete. It was possible to monitor the progress of the reaction by nmr since the olefinic methylene hydrogens of both allyl bromide and the product as well as the alcohol proton of perfluoro-t-butyl alcohol were well separated and well downfield from the large acetone peak.

The precipitated salt was removed by filtration and, upon addition of the acetone solution to water, a stable emulsion formed. This emulsion was extracted three times with toluene. The toluene solution was dried over anhydrous magnesium sulfate and fractionated at atmospheric pressure using a Vigreux column. The fractions boiling between 55 and 105° (44 ml) all contained product as well as acetone and a little toluene as the bp approached 105°. These fractions were combined, washed twice with water, dried over anhydrous magnesium sulfate, and again fractionated. Fraction 1, bp 73-78°, 15.8 g, contained 90% product (i.e. 14.2 g, 53%), 2% acetone, and 8% toluene. This material was not purified further but was used directly. Nmr (neat, disregarding solvent peaks, external TMS) 5.50 (1H, m, olefinic CH), 4.88 (2H, m, olefinic CH₂), 4.09 (2H, d, CH₂ next to oxygen); fmr 149.5 (sharp s, CF₃'s).

3-PERFLUORO-t-BUTOXYPROPYLTRICHLOROSILANE 22

To the above product containing 14.2 g (0.0514 mol) of allylperfluoro-t-butyl ether was added trichlorosilane (21.7 g, 0.160 mol) and 0.4 ml of an isopropanol solution containing 73 mg of chloroplatinic acid per millilitre. The solution was refluxed overnight and the excess trichlorosilane was removed by distillation. The residue was distilled and the clear colourless oil boiling at 82-86°/25 Torr was collected (18.4 g, 87%). Nmr (neat, external TMS) 4.02 (2H, t, CH₂ next to oxygen), 1.84 (2H, m, central propyl CH₂), 1.30 (2H, m, CH₂ next to silane).

3-PERFLUORO-t-BUTOXYPROPYLTRIETHOXYSILANE 9

Sodium (3.40 g, 0.148 gram atom), absolute ethanol (90 ml), and 3-perfluoro-t-butoxypropyltrichlorosilane (18.4 g, 0.0448 mol) were reacted and worked up using the procedure described for the synthesis of 5. A clear, colourless oil was collected at 90-93°/10 Torr (13.9 g, 71%). Nmr 3.88 (8H, q on top of a set of peaks, ethoxyl CH₂'s plus propyl CH₂ next to oxygen), 1.83 (2H, m, central propyl CH₂), 1.24 (9H, t, ethoxyl CH₃'s), 0.67 (2H, m, CH₂ next to silane); fmmr 149.7 (s, CF₃'s); n_D²⁵ 1.3559.

DICHLOROMETHYL-3-PERFLUORO-t-BUTOXYPROPYLSILANE

To allylperfluoro-t-butyl ether (3.68 g, 0.0133 mol) was added dichloromethylsilane (5.2 g, 0.0452 mol) and 0.10 ml of an isopropanol solution containing 73 mg of chloroplatinic acid per millilitre. The solution was refluxed overnight and the resultant reaction mixture was then distilled. The liquid boiling at 94-98°/41 Torr (4.53 g, 0.0116 mol, 87%) was the required product. Nmr 4.11 (2H, t, CH₂ next to oxygen), 1.92 (2H, m, central propyl CH₂), 1.20 (2H, m, CH₂ next to the silane), 0.82 (3H, s, silane CH₃).

DIETHOXYMETHYL-3-PERFLUORO-t-BUTOXYPROPYLSILANE 10

Sodium (1.02 g, 0.0443 gram atom), absolute ethanol (50 ml), and dichloromethyl-3-perfluoro-t-butoxypropylsilane (8.20 g, 0.0210 mol) were

reacted and worked up using the procedure described for the synthesis of 5. On distillation, a clear, colourless product bp 101-103°/30 Torr (2.64 g, 0.00644 mol, 31%) was obtained. Nmr (neat, external TMS) 3.83 (2H, t, propyl CH₂ next to oxygen), 3.56 (4H, q, ethoxyl CH₂'s), 1.58 (2H, m, central propyl CH₂), 0.97 (6H, t, ethoxyl CH₃'s), 0.39 (2H, m, propyl CH₂ next to silane), -0.15 (3H, s, CH₃ on silane); fmr 149.7 (s, CH₃'s); n_D^{25} 1.3574. The low yield in this reaction was most likely due to the unusually high humidity on that day. This is supported by the isolation from the reaction mixture of 1.90 g of a clear oil (bp 147-160°/10 Torr) which had an nmr consistent with that expected from the dimer.

NON-FLUORINATED MONOMERS AND POLYMERS FOR THE COPOLYMER STUDIES

Tetraethoxysilane, methyltriethoxysilane, polymethylhydrogensiloxane (molecular weight of about 3,500) and polydimethylsiloxane (viscosity 350 centistokes) were obtained commercially. The hexyl- and dodecyltriethoxysilanes were synthesized from the corresponding trichloro derivatives using the sodium ethoxide/ethanol technique described above.

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