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SYNTHESIS OF SPACE-STABLE
POLYMERIC FILM FORMERS
for
National Aeronautics & Space Administration
Langley Research Center
Langley Station
Hampton, Virginia 23365
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SYNTHESIS OF SPACE-STABLE POLYMERIC FILM FORMERS

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Prepared by
C. Giori

of
IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois 60616

for
National Aeronautics & Space Administration
Langley Research Center
Mail Stop 187
Langley Station
Hampton, Virginia 23365

Attention: Mr. W.S. Slemp

April, 1971
FOREWORD

This is report No. IITRI-C6216-7 (Final Report) on IITRI Project C6216, NASA-Langley Research Center Contract NAS1-10092, entitled, "Synthesis of Space-Stable Polymeric Film Formers." This report covers the period June 9, 1970 through January 8, 1971.

The work reported here has been conducted by Dr. C. Giori, Project Leader, with the technical assistance of Miss I. Lesевичius, Mr. P. Mencinskas and Mr. R.F. Boutin. Mr. G.A. Zerlaut provided technical consultation and administrative supervision.

Data are recorded in Logbooks Nos. C20085, C20181, C20234 and C20262.

The author wishes to acknowledge the cooperation and assistance of Mr. W.S. Slemp, the NASA-Langley Technical Monitor, and of Dr. Norman J. Johnston, also of NASA-Langley Research Center.

Respectfully submitted,
IIT RESEARCH INSTITUTE

Claudio Giori
Research Chemist
Polymer Chemistry Research

APPROVED:

G.A. Zerlaut
Manager
Polymer Chemistry Research

CG:jss
ABSTRACT

Several new fluoroaromatic silicon and carbon polymers have been synthesized and the effect of simulated solar ultraviolet and proton irradiation in a vacuum environment has been determined. The polymers studied are the s-triazinyl polyethers, the polyaryloxysiloxanes, the polydiphenylsiloxanes and Phenyl T ("ladder" polyphenylsilsesquioxane). Methods of synthesis and thermal properties of these polymers are described. Perfluorinated polymer structures have been successfully prepared. These polymers exhibit excellent stability to proton irradiation but are less stable to ultraviolet irradiation. It is suggested that the enhanced polarization of the carbon-silicon bonds due to the strong inductive effect of the perfluorophenyl groups is responsible for the relatively low ultraviolet and thermal stability of the perfluoroaromatic silicones.
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SYNTHESIS OF SPACE-STABLE POLYMERIC FILM FORMERS

I. INTRODUCTION

The requirements imposed on spacecraft thermal and space radiation protective surfaces by the long lifetimes of planned missions have necessitated the search for new and improved polymeric materials. New and/or improved polymers are required that are both highly transparent in the 0.2- to 2.7 \( \mu \) wavelength region and stable to the combined ultraviolet-plus-charged particle-radiation environment of deep space. These polymers are required for three separate, but related, surface coatings systems: (1) flexible substrates for second-surface mirrors; (2) sprayable and/or rigid solar-cell covers (film); and (3) binders for pigmented low \( \alpha_s/\epsilon \) (white) radiator surface coatings. It is to the first two requirements that emphasis was given in the work discussed herein.

The objective of this study was the synthesis and evaluation of new polymeric materials having potential utility as space-stable films for solar cell covers, second surface mirrors, or binders for thermal control coatings. The rationale for selection, the methods of synthesis, properties and the effects of simulated solar ultraviolet and proton irradiation on the polymers studied are described in the following paragraphs.
II. TECHNICAL BACKGROUND

Of the many transparent polymers that have been examined during the past 10 years, only the FEP Teflons and the 100% aliphatic polydimethylsiloxane elastomers and polymethylsiloxane resins have exhibited satisfactory optical stability to ultraviolet irradiation in vacuum. The poor processability of Teflons (TFE and FEP) have precluded their use in coatings and as solar cell covers, although they are being evaluated as substrates for flexible second-surface mirrors. However, in combined ultraviolet-plus-proton irradiation studies (4:4 acceleration factors for ultraviolet and H\(^+\)) recently performed at IITRI for COMSAT*, specimens of FEP-A second surface mirrors were observed to seriously degrade after only 1000 equivalent space hours.

We have synthesized thermally cured (i.e., non-catalyzed) polymethylsiloxane resins at IITRI that, when prepared as paints, compete with, if not exceed, the ultraviolet stability exhibited by the sodium and potassium silicate-based "water glass" analogs.

The energies of ultraviolet radiation, i.e., greater than 3.2 eV, are of the same order of magnitude as the chemical bonds present in polymers. Hence, ultraviolet degradation is bond selective and effects vary with wavelength. Chemically and structurally complicated polymers, e.g., epoxies, alkyds, polyurethanes, etc., possess functional groups with \(\sigma\)- and \(\pi\)-electron bonding and are strong ultraviolet absorbers; the more complicated the structure, the greater the absorption and the greater the probability of color formation.

While it is desirable to have simple, structurally uncomplicated polymers for optimum resistance to ultraviolet radiation in the space environment, this is thought to not necessarily be the case when low energy, charged-particle radiation is to be encountered simultaneously with ultraviolet radiation. Proton

*Performed for Mr. Carl Maag.

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and electron radiation are much less specific to chemical structure and, aside from any sputtering effects, charged-particle damage is related to the creation of secondary electrons along an ionization tract. The primary energy is dissipated as the secondary and succeeding generation electrons interact more and more with less tightly bound electrons. Eventually the valence electrons are ionized and electron-hole pairs result or organic bonds are broken, presumably by free radical mechanisms. It is important to note however that structure may be important on the basis of the cross-sectional area of the microstructure (i.e., atomic, molecular and ligand size) that presents itself as a target for statistical interaction with the "slowing" proton (or electron).

Because of the non-specificity of absorption of charged particles, except as noted above, it is not surprising that aromatic polymers have been shown to be more stable than their aliphatic analogs. This is attributed to the energy-sink effect of the high $\pi$-electron density and the shielding effect of the phenyl groups in the case of phenylated silicones and other systems. The energy-sink theory holds that stabilization is provided by the fact that second- and succeeding-generation electrons are largely precluded by the accommodation of any first-generation electrons in the electron-rich aromatic nuclei.

It was thought that the problem of preventing the primary ionization on interaction with a charged particle could be partially, if not largely, solved by replacing all, or an absolute maximum, of the labile hydrogens with fluorine. Then, if aromatic groups are strategically placed along the polymer backbone, either intramolecularly or as ligands, those first-generation electrons that are produced can be largely accommodated. It was believed that this would result in the maximization of stability of any given basic system to both charged particles (protons) and ultraviolet radiation. (In
the ultraviolet-induced excitation processes it is simply the labile hydrogen that is of most consequence and, in the presence of hydrocarbon, complete transparency to the ultraviolet has been the only solution, e.g., polydimethylsiloxane, Teflon and, to a much lesser extent, polymethylmethacrylate.)
III. RESULTS

A. s-Triazinyl Polyethers

The procedure employed for the synthesis of the s-triazinyl polyethers involves interfacial condensation of cyanuric chloride or 6-substituted 2,4-dichlorotriazine in nitrobenzene solution with an aromatic diol in sodium hydroxide solution in presence of a cationic emulsifier (Ref. 1);

\[
\begin{align*}
\text{Cl} & \quad \text{N} & \quad \text{N} & \quad \text{Cl} + \text{OH-} & \quad \text{R-OH} \quad \text{Interf.} \quad \begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{N} \\
\text{R'} \\
\text{N} \\
\text{N} \\
\text{R'} \\
\text{O-} \\
\end{array} \\
\end{align*}
\]

(1)

At low temperatures, the third chlorine of cyanuric chloride reacts with difficulty and linear polymers can be obtained. Cyanuric chloride and dichlorotriazine derivatives are less sensitive to hydrolysis than the dicarboxylic acid chlorides, and an amount of sodium hydroxide larger than that stoichiometrically required can be used to accelerate the reaction.

The reaction was first studied by using hydroquinone and bisphenol A as the diols and cyanuric chloride as the condensing agent. Hydroquinone formed a yellow-brown polymer insoluble in all organic solvents. No melting point was observed to 300°C (Table 1, Polymer 1). Bisphenol A formed a white polymer that softened at 140-240°C, was soluble in several organic solvents, and formed clear films (Table 1, Polymer 2). The difference in solubility and melting point of these two polymers is probably due to the higher rigidity of the polymer structure based on hydroquinone, compared to that of bisphenol A.

Tetrafluorohydroquinone is much less reactive than hydroquinone. Because of the electron withdrawing effect of substituted fluorine, the electronegativity of the phenoxide ion is decreased. This increases the acidity of the phenolic group (the less negative the oxygen, the greater the repulsion of the proton) and decreases its nucleophilic character. In this case,
Table 1
STRUCTURE AND GENERAL PROPERTIES OF THE S-TRIAZINYL POLYETHERS SYNTHESIZED

<table>
<thead>
<tr>
<th>Polymer Composition</th>
<th>Color</th>
<th>Solubility</th>
<th>Formability</th>
<th>Softening Point °C</th>
<th>Polymer No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Chemical Structure 1]</td>
<td>Yellow-Brown</td>
<td>Insoluble</td>
<td></td>
<td>&gt;300</td>
<td>1</td>
</tr>
<tr>
<td>![Chemical Structure 2]</td>
<td>White</td>
<td>Chloroform and others</td>
<td>+</td>
<td>140</td>
<td>2</td>
</tr>
<tr>
<td>![Chemical Structure 3]</td>
<td>Yellow</td>
<td>Hexamethyl-phosphoramid(*)</td>
<td>-</td>
<td>&gt;300</td>
<td>3</td>
</tr>
<tr>
<td>![Chemical Structure 4]</td>
<td>White</td>
<td>Chloroform and others</td>
<td>+</td>
<td>225</td>
<td>4</td>
</tr>
<tr>
<td>![Chemical Structure 5]</td>
<td>White</td>
<td>Chloroform and others</td>
<td>+</td>
<td>170</td>
<td>5</td>
</tr>
<tr>
<td>![Chemical Structure 6]</td>
<td>Light Grey</td>
<td>Hexamethyl-phosphoramid(*)</td>
<td>-</td>
<td>&gt;300</td>
<td>6</td>
</tr>
</tbody>
</table>

(*) With discoloration.
an excess of sodium hydroxide and a higher reaction temperature result in a higher yield of polymer. The same reaction with cyanuric chloride at 6-7°C resulted in 84% yield with hydroquinone and only 24% with tetrafluorohydroquinone. The yield of the tetrafluorohydroquinone polymer increased (44%) by operating at ambient temperature. Even higher yield (60%) was obtained at ambient temperature by using double the amount of sodium hydroxide in the aqueous phase.

If tetrafluorohydroquinone is substituted for hydroquinone, the solubility of the resulting polymer is improved. The polymer obtained from cyanuric chloride and tetrafluorohydroquinone (Table 1, Polymer 3), although insoluble in most solvents, is partially soluble in N-methyl pyrrolidone and N,N-dimethylacetamide and completely soluble in hexamethylphosphoramidate. However, these solutions develop a very dark color, probably because of a side reaction between the amide-type solvent and the unreacted chlorine of the triazine unit. The color does not improve on drying. To overcome this problem, we studied the synthesis of s-triazinyl polyethers from 2,4-dichloro 6-substituted triazines. One chlorine of cyanuric chloride is replaced by an unreactive substituent and polymers essentially chlorine-free can be obtained. The 2,4-dichloro 6-phenyl triazine was therefore polymerized with bisphenol A or hexafluorobisphenol A (Table 1, Polymers 4 and 5), e.g.:

\[
\text{Cl-} \begin{array}{c} \text{N} \\
\text{Cl} \\
\text{N} \\
\text{Cl} \\
\text{N}
\end{array} + \begin{array}{c} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3
\end{array} \rightarrow 
\begin{array}{c} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3 \\
\text{C} \text{-} \text{O} \text{-} \text{CF}_3
\end{array}
\]
The polymers obtained are soluble and form clear films. The effect of simulated solar ultraviolet and proton irradiation on the 6-phenyl 2,4-triazinyl polyether obtained with hexafluoro-bisphenol A was determined. The polymer is very stable to proton irradiation, but is degraded by ultraviolet irradiation (Table 2).

Since our final objective was the preparation of a completely fluorinated triazinyl polyether, the synthesis of new perfluorinated triazine derivatives was undertaken. In particular, we studied the synthesis of 2,4 dichloro 6-(pentafluorophenyl)triazine and 2,4-dichloro 6-(pentafluorophenoxy)triazine:

![Chemical structures](image)

The methods employed for the synthesis were similar to those described for the analogous unfluorinated materials (Ref. 2). A Grignard method was employed for the synthesis of the 2,4-dichloro 6-(pentafluorophenyl)triazine. Pentafluorochlorobenzene was used initially but the more reactive pentafluorobromobenzene was preferred in successive experiments.

![Synthesis reactions](image)
Table 2

Effect of proton and ultraviolet irradiation in vacuum on the reflectance of a triazinyl polyether obtained from hexafluorobisphenol A and 6-phenyl 2,4-dichlorotriazine.

<table>
<thead>
<tr>
<th>Wavelength (micron)</th>
<th>Proton Irradiation$^a$ -ΔR(%)</th>
<th>Ultraviolet Irradiation$^b$ -ΔR(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.325</td>
<td>2.5</td>
<td>38</td>
</tr>
<tr>
<td>0.35</td>
<td>1.5</td>
<td>36</td>
</tr>
<tr>
<td>0.40</td>
<td>&lt;1.0</td>
<td>27</td>
</tr>
<tr>
<td>0.45</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>0.50</td>
<td>&lt;1.0</td>
<td>11</td>
</tr>
<tr>
<td>0.55</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>0.60</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>0.65</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>0.70</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$Fluence of $1.4 \times 10^{15}$ protons/cm$^2$ with an energy of 1.2 kev.

$^b$500 equivalent sun hours of ultraviolet irradiation.
The product obtained is a yellow material, M.P. 120-135°C, that sublimes rapidly at 60°C. It is unstable and becomes oily on standing. No polymerization studies have been conducted with this intermediate.

The 2,4-dichloro 6-(pentafluorophenoxy)triazine was prepared from pentafluorophenol and cyanuric chloride by a Schotten-Baumann reaction:

\[
\text{OH} + \begin{array}{c} \text{Cl} \end{array} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{N} \end{array} \rightarrow \begin{array}{c} \text{Cl} \end{array} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{Cl} \end{array}
\]

(5)

The reaction was conducted by dropwise addition of an aqueous solution of pentafluorophenol containing a stoichiometric amount of sodium hydroxide to a stirred solution of cyanuric chloride in chloroform. The vacuum sublimed product was white, M.P. = 92-94°C. This was polymerized with tetrafluorohydroquinone to form a perfluorinated triazinyl polyether:

\[
\begin{array}{c} \text{Cl} \end{array} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{Cl} \end{array} + \begin{array}{c} \text{OH} \end{array} \begin{array}{c} \text{F} \end{array} \begin{array}{c} \text{O} \end{array} \rightarrow \begin{array}{c} \text{F} \end{array} \begin{array}{c} \text{F} \end{array} \begin{array}{c} \text{O} \end{array} \begin{array}{c} \text{F} \end{array}
\]

(6)

A light-grey polymer was obtained, not melting to 300°C (Table 1, Polymer 6). The polymer is insoluble in all organic solvents and is only slightly soluble in hexamethylphosphoramide. No films could be obtained and the effect of ultraviolet and proton ir-radiation was not determined. The thermal stability of this polymer by TGA was surprisingly low (Figure 1).
Figure 1: THERMOGRAVIMETRIC ANALYSIS OF A PERFLUORINATED TRIAZINYL POLYETHER OBTAINED FROM TETRAFLUOROHYDROQUINONE AND 2,4-DICHLORO 6-(PENTAFLUOROPHENOXY)TRIAZINE IN NITROGEN (CONTINUOUS LINE) AND AIR (DOTTED LINE). RATE OF HEATING = 10°/MIN.
B. Polyaryloxysiloxanes

A new method of polymerization in solution has been developed for the synthesis of high molecular weight polyaryloxysiloxanes. This method has the advantage over the previously reported melt polymerization method (Ref. 3, 4) in that completely colorless polymers can be obtained. The method is based on the direct condensation of diphenyldichlorosilane with an aromatic diol in 1,2-dichlorobenzene solution at 0°C in the presence of triethylamine. Hydroquinone has been used as the diol:

\[
\begin{align*}
\text{Cl-Si-Cl} + \text{OH-} & \xrightarrow{\text{Et}_3\text{N}} \text{Si-O} - \text{O-} + \text{Et}_3\text{N-} \cdot \text{HCl} \\
\end{align*}
\]

Dichlorobenzene is the most suitable solvent for this reaction. Toluene, methyl chloride, dimethylacetamide (with and without triethylamine) gave lower molecular weights and lower yields because polymer precipitation occurred during polymerization. Colorless, transparent films could be obtained by casting from 1,2-dichlorobenzene solutions.

Differential thermal analysis of this polyaryloxysiloxane showed, as expected, no endotherms up to 400°C, indicating the absence of transition temperatures or crystalline melting point. The polymer softens in the range 130-195°C, higher than previously reported (65-70°C; Ref. 4). Ultraviolet transmission measurements in a solution of spectrophotometric N,N-dimethylacetamide showed that the polymer is transparent at wavelengths higher than 0.3μ (Figure 2). Simulated solar ultraviolet irradiation experiments were conducted and pre- and post-irradiation reflectance was measured. A decrease in reflectance was observed in the ultraviolet and visible range (Table 3).
FIGURE 2: ULTRAVIOLET TRANSMISSION OF A POLYARYLOXYSILOXANE OBTAINED FROM HYDROQUINONE AND DIPHENYLDICHLOOROSILANE MEASURED IN DIMETHYLACETAMIDE SOLUTION (0.05% WT).
Table 3

Effect of ultraviolet irradiation in vacuum on the reflectance of a polyaryloxysiloxane obtained from hydroquinone and diphenyldichlorosilane.

<table>
<thead>
<tr>
<th>Wavelength (micron)</th>
<th>Ultraviolet Irradiation&lt;sup&gt;a&lt;/sup&gt; -ΔR(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.325</td>
<td>22</td>
</tr>
<tr>
<td>0.35</td>
<td>24</td>
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<tr>
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<td>22</td>
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<tr>
<td>0.65</td>
<td>2</td>
</tr>
<tr>
<td>0.70</td>
<td>1.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>1000 equivalent sun hours of ultraviolet irradiation.
The thermal stability of this polymer was measured by TGA in nitrogen and air (Figure 3). In nitrogen, decomposition starts at about 360°C; in air, only a 2% weight loss is observed at this temperature.

The polymerization procedure described above cannot be applied when tetrafluorohydroquinone is substituted for hydroquinone. This is due to the low reactivity of tetrafluorohydroquinone in nucleophilic displacements, also observed in the synthesis of triazinyl polyethers from this perfluorinated diol. Solution polymerization experiments were conducted at 0°C, ambient temperature, 50°C, 80°C. These experiments were not successful because of the low reactivity of tetrafluorohydroquinone at low temperatures (0-25°C) and the occurrence of side reactions with the solvent or the acid acceptor at higher temperatures. Better results were obtained by melt polymerization. Tetrafluorohydroquinone and diphenyldichlorosilane were mixed at room temperature and slowly heated up to 170°C with stirring under nitrogen flow:

\[
\begin{align*}
\text{Cl-Si-Cl} + \text{OH} & \rightarrow \text{Si-O-} \\
\text{F} & \rightarrow \text{F}
\end{align*}
\]

Hydrochloric acid was evolved. After 12 hr a viscous, unstirrable melt was obtained and evolution of hydrochloric acid was complete. The polymer obtained was soluble with difficulty in toluene and 1,2-dichlorobenzene and was more soluble in amide-type solvents. Films that were almost colorless could be cast from these solutions.

Since our final objective was the synthesis of a completely fluorinated silicon polymer, our attention was therefore devoted to the synthesis of intermediate perfluorophenylsilanes that could be used for the synthesis of perfluorinated silicon polymers.
FIGURE 3: THERMOGRAMMETRIC ANALYSIS OF A POLYARYLOXYDOSILXANE OBTAINED FROM HYDROQUINONE AND DIPHENYLDICHLOROSILANE IN NITROGEN (CONTINUOUS LINE) AND AIR (DOTTED LINE). RATE OF HEATING = 10°C/MIN.
polyaryloxy-siloxanes (by condensation with tetrafluorohydroquinone) as well as perfluorophenyl silicone resins (by hydrolytic polymerization).

C. Polydiphenylsiloxane and Phenyl T

Because of the expense involved in the synthesis of perfluorosilane monomers, before studying the synthesis of the analogous perfluorinated polymers we studied the synthesis of the unfluorinated polydiphenylsiloxane and Phenyl T.

Polydiphenylsiloxane was prepared by hydrolytic polymerization of the diphenyldichlorosilane:

\[
\text{Cl-Si-Cl} \rightarrow [\text{Si-O-}]_n
\]

The diphenyldichlorosilane was dissolved in toluene and the solution was shaken with excess of water. The white resin obtained was cured for 16 hr at 195°C. It could be dissolved in organic solvents and formed clear films. The polymer is low melting (M.P. = 72°C) but stable at higher temperatures in the molten state. Thermogravimetric analysis shows that the decomposition starts near 300°C with a 5% weight loss at about 365°C (Figure 4).

Phenyl T (General Electric's trade name for "ladder" polyphenylsilesesquioxane) is obtained by hydrolytic polymerization of phenyltrichlorosilane:

\[
\text{PhSiCl}_3 \rightarrow [\text{Si-O-Si-O-}]_n
\]
FIGURE 4: THERMOGRAVIMETRIC ANALYSIS IN NITROGEN OF POLYDIPHENYLSILOXANE.
RATE OF HEATING = 10°C/MIN.
It has been reported (Ref. 5) that Phenyl T can be prepared by equilibration near 250°C of a highly concentrated solution of the product of hydrolysis of trichlorophenylsilane. Trichlorophenylsilane was dissolved in toluene and hydrolyzed with water. Evaporation of toluene by slowly heating the hydrolysate solution to 259°C and equilibration at this temperature at 80% concentration in benzophenone followed by addition of benzene and precipitation with methanol gave an infusible polymer soluble in benzene that could form clear but brittle films. Thermogravimetric analysis (Figure 5) shows that under nitrogen decomposition starts near 400°C with a 5% weight loss at 510°C. A very stable residue is formed (only 23% weight loss at 850°C).

The effect of ultraviolet and proton irradiation in vacuum was determined on pigmented and unpigmented samples of both polymers. These polymers are very stable to proton irradiation, whereas ultraviolet irradiation causes a decrease in reflectance (Tables 4 and 5).

D. Polydi(pentafluorophenyl)silane and Perfluorinated Phenyl T

These polymers differ from the ones described in the previous section in that the phenyl groups are perfluorinated.

The synthesis of the intermediate difunctional and trifunctional pentafluorophenylsilanes is complicated by several factors. We attempted the direct synthesis of the dichloro and trichloro(pentafluorophenyl)silane from silicon tetrachloride and pentafluorophenylbromide in anhydrous ether via Grignard formation:

\[
\begin{align*}
\text{Br} & \quad + \quad \text{Mg} \\
\text{F} & \quad \xrightarrow{\text{MgBr}} \\
\text{SiCl}_4 & \quad \xrightarrow{\text{F-MgBr}} \\
& \quad \text{F-SiCl}_3 & \quad \xrightarrow{\text{F-MgBr}} \\
& \quad (\text{F})_2\text{SiCl}_2
\end{align*}
\]

(11)
FIGURE 5: THERMOGRAVIMETRIC ANALYSIS IN NITROGEN OF PHENYL T.
RATE OF HEATING = 10°C/MIN.
Table 4

Effect of proton and ultraviolet irradiation in vacuum on the reflectance of polydiphenylsiloxane.

<table>
<thead>
<tr>
<th>Wavelength (micron)</th>
<th>Unpigmented Sample</th>
<th>Pigmented Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proton Irradiation $^a$</td>
<td>Ultraviolet Irradiation $^b$</td>
</tr>
<tr>
<td>0.325</td>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>0.35</td>
<td>&lt;1</td>
<td>22</td>
</tr>
<tr>
<td>0.40</td>
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</tr>
<tr>
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<td>14</td>
</tr>
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</tr>
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</tr>
<tr>
<td>0.70</td>
<td>0</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

$^a$Fluence of $1.4 \times 10^{15}$ protons/cm$^2$ with an energy of 1.2 kev.

$^b$500 equivalent sun hours of ultraviolet irradiation.
Table 5

Effect of proton and ultraviolet irradiation in vacuum on the reflectance of Phenyl T

<table>
<thead>
<tr>
<th>Wavelength (micron)</th>
<th>Unpigmented sample</th>
<th>Pigmented Sample, Ultraviolet Irradiation</th>
<th>Pigmented Sample, Ultraviolet Irradiation</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>Ultraviolet Irradiation(^b)</td>
<td>Ultraviolet Irradiation(^b)</td>
</tr>
<tr>
<td>0.325</td>
<td>4</td>
<td>33</td>
<td>&lt;1</td>
</tr>
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<td>3</td>
<td>30</td>
<td>&lt;1</td>
</tr>
<tr>
<td>0.40</td>
<td>1</td>
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</tr>
<tr>
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</tr>
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<td>9</td>
</tr>
<tr>
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<tr>
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<td>0</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>0.65</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0.70</td>
<td>0</td>
<td>&lt;1</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^a\) Fluence of 5.2 \times 10^{15} \text{protons/cm}^2 \text{ with an energy of 1.2 kev.}

\(^b\) 500 equivalent sun hours of ultraviolet irradiation.
The normal procedure of adding the preformed Grignard reagent in ether to tetrachlorosilane is not suitable. Even by using a large excess of silicon tetrachloride, the main reaction product is the tetra(pentafluorophenyl)silane (Ref. 6). This has been explained (Ref. 7) on the basis that once a pentafluorophenyl group is introduced, the reactivity of the remaining chlorine atom attached to the silicon is enhanced and further replacement is rapid to give the fully substituted silane. To overcome this problem, a modified procedure has been suggested (Ref. 8) in which the Grignard reagent is formed and reacted "in-situ." However, in spite of several attempts we could not prepare the dichloro and trichloro(pentafluorophenyl)silane in the yield reported. Only traces of these products were obtained. The reaction was complicated by the instability of pentafluorophenylmagnesium bromide that decomposes and forms insoluble and infusible para-substituted condensation products. The tendency of pentafluoro-phenylmagnesium bromide to decompose is known (Ref. 9) and the rate of decomposition is increased by the presence of tetrachlorosilane (Ref. 7).

A different procedure was studied. A mixture of ethoxychlorosilanes, prepared from ethanol and tetrachlorosilane at 1.8/1 molar ratio (Ref. 10), was reacted in ether at -78°C with pentafluorophenylmagnesium bromide in an amount stoichiometrically equivalent to the chlorine atoms present. The mixture was slowly heated to room temperature under stirring. Two products were isolated, B.P. 55-58°C and 86-89°C at 1.5 mm, that appear to be the pentafluorophenyldiethoxysilane and the di(pentafluorophenyl) ethoxychlorosilane. The yield was quite low, and the by-products from the decomposition of the Grignard reagent constituted the main product of the reaction.

The Grignard synthesis is easier if pentafluorophenylmagnesium bromide is reacted with tetraethoxysilane. The pentafluorophenyltriethoxysilane and the di(pentafluorophenyl)diethoxysilane can be obtained:
Although tetraethoxysilane is less reactive than the chlorosilanes toward Grignard reagents, it does not promote the decomposition of pentafluorophenylmagnesium bromide like the chlorosilanes. Besides, the reactivity of the partially substituted ethoxysilanes is not enhanced as are the chlorosilanes, and the diethoxy and triethoxy(pentafluorophenyl)silanes can be obtained.

These ethoxysilanes were successfully polymerized. They can be hydrolyzed with dilute hydrochloric acid and there is no need to convert them into the chlorosilanes. The products of the hydrolysis are the pentafluorophenylsilanols that polymerize spontaneously:

\[
\begin{align*}
\text{Si(OEt)}_4 & \xrightarrow{\text{MgBr}} \text{Si(OEt)}_3 \\
\text{Si(OEt)}_3 & \xrightarrow{\text{MgBr}} (\text{SiO})_2\text{Si(OEt)}_2 \\
\end{align*}
\]
The main difference with the hydrolysis and polymerization of the analogous unfluorinated monomers is the tendency of the pentafluorophenylsilanes to form insoluble gels, particularly when the triethoxy(pentafluorophenyl)silane is used. Therefore it is necessary to operate in the presence of an organic solvent, at low concentration of the reactants and at low reaction temperatures. The silane was dissolved in toluene and hydrolyzed with dilute hydrochloric acid. The hydrolysis was followed by IR analysis and was considered complete when the IR spectra showed an absence of the C-H absorption band (due to the presence of ethoxy groups). Hydrolysis and polycondensation occur in one step. As hydroxyl groups are generated by hydrolysis, polycondensation takes place. This procedure results in the formation of soluble, film-forming polymers. Only traces of insoluble, infusible product were obtained from the triethoxy(pentafluorophenyl)silane. If the hydrolysis of the triethoxy(pentafluorophenyl)silane is conducted in dilute hydrochloric acid in the absence of organic solvent, the hydrolysis is faster, but a gel that is only partially soluble in DMSO is obtained.

Simulated solar ultraviolet and proton irradiation experiments were conducted on pigmented and unpigmented samples of both polymers. These polymers show good stability to proton irradiation. A decrease in reflectance is observed after exposure to ultraviolet irradiation (Tables 6 and 7).

Thermal properties of both polymers have been studied by thermal analysis in nitrogen. Decomposition of the polydi(pentafluorophenyl)siloxane starts at about 220°C with a 5% weight loss at 300°C (Figure 6). Decomposition of the perfluorinated Phenyl T starts at about 350°C with a 5% weight loss at 465°C (Figure 7).
Table 6

Effect of proton and ultraviolet irradiation in vacuum on the reflectance of polydi(pentafluorophenyl)siloxane.

<table>
<thead>
<tr>
<th>Wavelength (micron)</th>
<th>Unpigmented Sample</th>
<th>Pigmented Sample, Ultraviolet Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proton Irradiation</td>
<td>Ultraviolet Irradiation</td>
</tr>
<tr>
<td></td>
<td>-ΔR(%)(^a)</td>
<td>-ΔR(%)</td>
</tr>
<tr>
<td>0.325</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>0.35</td>
<td>2</td>
<td>7</td>
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<td>0.40</td>
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<td>3.5</td>
</tr>
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<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0.60</td>
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<tr>
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<td>0</td>
</tr>
<tr>
<td>0.70</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)Fluence of $1.8 \times 10^{15}$ protons/cm\(^2\) with an energy of 1.2 kev.

\(^b\)Fluence of $5.4 \times 10^{15}$ protons/cm\(^2\) with an energy of 1.2 kev.

\(^c\)500 equivalent sun hours of ultraviolet irradiation.
Table 7

Effect of proton and ultraviolet irradiation in vacuum on the reflectance of perfluorinated Phenyl T.

<table>
<thead>
<tr>
<th>Wavelength (micron)</th>
<th>Unpigmented Sample</th>
<th>Pigmented Sample, Ultraviolet Irradiation</th>
</tr>
</thead>
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<tr>
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<td>Proton Irradiation $^a$ -ΔR(%)</td>
<td>Ultraviolet Irradiation $^b$ -ΔR(%)</td>
</tr>
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<td>0.55</td>
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<td>2.5</td>
</tr>
<tr>
<td>0.70</td>
<td>0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$Fluence of $5.2 \times 10^{15}$ protons/cm$^2$ with an energy of 1.2 kev.

$^b$500 equivalent sun hours of ultraviolet irradiation.
FIGURE 6: THERMOGRAVIMETRIC ANALYSIS IN NITROGEN OF POLYDI(PENTAFLUOROPHENYL) SILoxane. RATE OF HEATING = 10°C/MIN.
FIGURE 7: THERMOGRAVIMETRIC ANALYSIS IN NITROGEN OF PERFLUORINATED PHENYL T.
RATE OF HEATING = 10°C/MIN.
IV. EXPERIMENTAL

A. Synthesis of s-Triazinyl Polyethers

1. Intermediates

2,4-dichloro 6-(pentafluorophenoxy)triazine. To a solution of cyanuric chloride (18.5g) in the minimum amount of chloroform sufficient to dissolve it, a solution of pentafluorophenol (20.4g) and sodium hydroxide (4.5g) in water (5cc) was added dropwise with stirring. An exothermic reaction was observed. After completing the addition, the mixture was heated to 50°C and maintained at this temperature for 1 hr. The chloroform phase was separated, washed with dilute sodium hydroxide, then with water, and dried over anhydrous calcium chloride. After filtration and distillation of the chloroform, the product obtained was purified by vacuum sublimation. The 2,4-dichloro 6-(pentafluorophenoxy)triazine obtained was a white material, M.P. 92-94°C (% calc. for C₉N₃Cl₂F₅O: C = 32.5, N = 12.6, Cl = 21.4, F = 28.6; % found: C = 33.6, N = 13.0, Cl = 20.9, F = 28.5, H = absent).

2,4-dichloro 6-(pentafluorophenyl)triazine. To a solution of cyanuric chloride (18.44g) in benzene (80cc), a Grignard solution prepared from pentafluorobromobenzene (39.5g) and magnesium (3.89g) in ether (40cc) was added while cooling with ice and stirring. After distillation of the solvents, the residue was extracted with petroleum ether. The petroleum ether was distilled and the residue was sublimed under vacuum. The product obtained was white but turned yellow shortly after sublimation (M.P. 120-135°C). It appears that the product decomposes on standing. No polymerization studies have been conducted with this intermediate.

2. Polymerization

The procedure generally employed was an interfacial polymerization method in the presence of a cationic emulsifier. Two emulsifiers were evaluated: Lauryl pyridinium chloride (Hooker) and Emcol cc-9 (Witco). Both were satisfactory but Emcol cc-9 (a liquid quaternary ammonium chloride) was preferred because
of its better color. Alkaline solutions of hydroquinone or tetrafluorohydroquinone discolor very rapidly. When these diols are used it is important to operate under rigorously inert atmosphere and to react these solutions immediately after preparation.

The following procedure was employed for the synthesis of polymers 1 and 2 (Table 1). Cyanuric chloride (0.009 mole) was dissolved in nitrobenzene (19.5 cc). A solution of the aromatic diol (0.009 mole), sodium hydroxide (0.018 mole), and Emcol cc-9 (0.9 g) in water (30 cc) was rapidly added to the cyanuric chloride solution with vigorous stirring at 6-7°C. After 5 hr the pH of the aqueous phase was about 7. The organic phase was separated and coagulated with excess of acetone. The polymer was collected by filtration, washed repeatedly with acetone, water and methanol, and dried under vacuum.

The same procedure was used for the synthesis of polymers 3 and 6 (Table 1) but the reaction was conducted at room temperature respectively with 0.036 and 0.027 mole of sodium hydroxide. The composition of polymer 6 (Table 1), a perfluorinated triazinyl polyether from tetrafluorohydroquinone and 2,4-dichloro 6-(pentafluorophenoxy)-triazine was confirmed by IR analysis (Figure 8) and elemental analysis (% calc for C_{15}N_{3}O_{3}F_{9}; C = 41, N = 9.5, F = 39; % found: C = 41.4, N = 8.55, F = 39).

A modified procedure was employed for the synthesis of polymers 4 and 5 (Table 1). 2,4-Dichloro 6-phenyltriazine (0.009 mole) and the aromatic diol (0.009 mole) were dissolved in nitrobenzene (39 cc). A solution of sodium hydroxide (0.009 mole) and Emcol cc-9 (0.9 g) in water (40 cc), saturated with sodium chloride, was added at 6°C with stirring. Stirring was continued until the aqueous phase was neutral (45 min). The temperature was raised to 15°C, 4.5 cc of sodium hydroxide 2N saturated with sodium chloride was added and stirring continued until the aqueous phase was neutral (2 hr). Another addition of sodium hydroxide was made at this point (4.5 cc of sodium
FIGURE 8: INFRARED SPECTRUM OF A PERFLUORINATED TRIAZINYL POLYETHER OBTAINED FROM TETRAFLUOROHYDROQUINONE AND 2,4-DICHLORO 6-(PENTAFLUOROPHENOXO)TRIAZINE.
hydroxide 2N) and stirring was continued for three more hours. The organic phase was separated and coagulated in excess of methanol. The polymer was filtered, washed with water and methanol and dried under vacuum.

B. Synthesis of Polyaryloxysiloxanes

Polycondensation of diphenyldichlorosilane with hydroquinone.
The procedure employed is a low temperature solution polycondensation. Hydroquinone (0.05 mole, 5.50g) is added to a solution of triethylamine (1.05 mole, 10.62g) in 1,2-dichlorobenzene (37.5cc). Hydroquinone does not dissolve and the color of the solution turns blue. To this suspension, a solution of diphenyldichlorosilane (0.05 mole, 12.66g) in 1,2-dichlorobenzene is added dropwise over a period of 1 hr with stirring under nitrogen at 0°C. The blue color gradually fades as the viscosity of the solution increases. Complete reaction of hydroquinone is indicated by the disappearance of all solid particles. Near the end of the addition the solution becomes too viscous to allow efficient stirring and dichlorobenzene (25cc) is added. At this point the solution is clear and colorless. The solution is slowly heated to room temperature and stirring continued for 1 hr. The solution is poured into an excess of methanol, the polymer filtered, washed repeatedly with methanol and dried under vacuum. The polymer obtained is white (11.9g; yield=82%). The structure of this polymer was confirmed by IR analysis (Figure 9) and elemental analysis (% calculated for C_{18}H_{14}SiO_2: C=74.5, H=4.8; % found: C=73.5, H=4.8). The inherent viscosity determined at 25°C for a solution of 0.5g/100cc of chlorobenzene was 0.36.

Polycondensation of diphenyldichlorosilane with tetrafluoro-hydroquinone. Tetrafluorohydroquinone (0.025 mole, 4.55g) and diphenyldichlorosilane (0.025 mole, 6.33g) were mixed at room temperature and slowly heated up to 170°C in a flask equipped with stirrer, nitrogen inlet and outlet. The gas outlet had a fritted glass disc to allow evolution of gases while preventing sublimation of tetrafluorohydroquinone. Hydrochloric acid was
Figure 9: Infrared spectrum of a polyaryloxysiloxane obtained from hydroquinone and diphenyl dichlorosilane.
evolved. After approximately 12 hr at 170°C a viscous unstirrable melt was obtained. Evolution of hydrochloric acid was complete at this point. The polymer obtained was grey. Opaque films were obtained from dimethylacetamide solutions that became clear on heating at 100°C.

C. Synthesis of Polydiphenylsiloxane

Diphenyldichlorosilane (12g) in toluene (8.5g) was added to water (50cc) with stirring. The white product obtained was isolated and washed several times with water until the aqueous phase was neutral, indicating that hydrolysis was complete. The product obtained was a low molecular weight polysiloxane. This was heated at 120°C to allow evaporation of the toluene and water present and further polymerized at 195°C for 16 hr. A clear, film forming polymer was obtained that was soluble in several organic solvents, including chloroform, toluene and tetrahydrofurane.

D. Synthesis of Phenyl T

Trichlorophenylsilane (50cc) in benzene (50cc) was added to water (100cc) with stirring. The gluey organic layer was separated and washed with water until the aqueous phase was acid-free. A portion of the organic layer (2.25g, solid content 52%) was added to benzophenone (0.32g). The mixture was heated slowly to 259°C by using a diphenylether vapor bath. Benzene and traces of water present were slowly distilled. The residue was equilibrated by heating at 259°C for 1.5 hr. Benzene (3.5cc) was added and the solution precipitated in excess of methanol. The polymer was filtered and dried under vacuum. The polymer obtained (1.03g; yield = 88%) was soluble in benzene and formed clear but brittle films.
E. Synthesis of Polydi(pentafluorophenyl) siloxane and Perfluorinated Phenyl T

1. Intermediate Di(pentafluorophenyl) diethoxysilane and Pentafluorophenyltriethoxysilane

Although the yields were rather low, these materials could be satisfactorily prepared via Grignard synthesis (Ref. 8). Pentafluorobromobenzene (0.5 mole, 123.5g), magnesium turnings previously washed with anhydrous ether and dried in vacuum (0.55 mole, 13.25g) and tetraethoxysilane (0.5 mole, 104g) were mixed at room temperature in a flask equipped with mechanical stirrer and condenser. Ethyl ether (previously dried over sodium) was added dropwise to the vigorously stirred mixture. When approximately 100cc of ether was added, an exothermic reaction was observed indicating the formation of the Grignard reagent. Stirring and refluxing was continued for 24 hr. The solution was cooled to room temperature and an excess of n-heptane was added to precipitate the magnesium salts. The solution was filtered under vacuum (by-products of the decomposition of the Grignard reagent were present in the filtrate along with magnesium salts and unreacted magnesium). Solvents and unreacted tetraethoxysilane were removed by distillation and the residue was fractionally distilled to give pentafluorophenyltriethoxysilane, 25g, B.P. = 68-69°C (1.5 mm), and di(pentafluorophenyl) diethoxysilane, 12g, B.P. = 83-84°C (1.5 mm).

The pentafluorophenyltriethoxysilane could be obtained in higher yield (38g) by using an excess of tetraethoxysilane (2 mole, 416g). However, the excess of tetraethoxysilane reduced the yield of di(pentafluorophenyl) diethoxysilane and only traces of this product were obtained. When an excess of tetraethoxysilane was used, it was necessary to use at least 300cc of ether and to add a few drops of methyl iodide to start the reaction. No. by-products due to the decomposition of the Grignard were observed, indicating that the decomposition of the Grignard reagent is reduced by an excess of tetraethoxysilane.
The yield of di(pentafluorophenyl)diethoxysilane can be increased by decreasing the concentration of tetraethoxysilane, but regardless of the ratio of tetraethoxysilane/Grignard reagent, the main product of the reaction is always the pentafluoro-phenyltriethoxysilane.

The IR spectra of the di(pentafluorophenyl)diethoxysilane and pentafluorophenyltriethoxysilane are shown in Figures 10 and 11. As expected, the relative intensities of the C-H absorption band (2980 cm⁻¹) and pentafluorophenyl absorption band (1640 cm⁻¹) are different in the two spectra. The composition of these intermediates was also confirmed by elemental analysis (% calculated for C₁₆H₁₀₂SiF₁₀: C = 42.5, H = 2.2, F = 42; % found: C = 43.1, H = 2.7, F = 41.3. % calculated for C₁₂H₁₅₃SiF₅: C = 43.7, H = 4.5, F = 28.8; % found: C = 43.9, H = 4.7, F = 28.7).

2. Hydrolytic Polymerization of Di(pentafluorophenyl)diethoxysilane

Di(pentafluorophenyl)diethoxysilane (1g) was dissolved in toluene (3g) and the solution added to water (2g) containing one drop of hydrochloric acid. The mixture was stirred at 50°C under nitrogen. The hydrolysis was followed by IR analysis, and it was considered complete when, by drying a few drops of the toluene layer on a sodium chloride window, no C-H absorption band (2980 cm⁻¹) was observed, indicating that ethoxy groups were absent. After 60 hr the hydrolysis was complete. The organic phase was separated and clear films could be obtained from the toluene solution. The IR spectrum of this polymer is shown in Figure 12, (% calculated for C₁₂F₁₀SiO: C = 38.1, F = 50.2; % found: C = 37.5, F = 48.6, H = 0.21).

3. Hydrolytic Polymerization of Pentafluorophenyltriethoxysilane

Pentafluorophenyltriethoxysilane (1g) was dissolved in toluene (5g) and the solution added to water (1g) containing one drop of hydrochloric acid. The hydrolysis was followed by IR analysis as described for the hydrolysis of the diethoxy derivative. After
FIGURE 11: INFRARED SPECTRUM OF PENTAFLUOROPHENYLTRIETHOXYSILANE
**FIGURE 12: INFRARED SPECTRUM OF POLYDI(PENTAFLUOROPHENYL) SILOXANE**
FIGURE 13: INFRARED SPECTRUM OF PERFLUORINATED PHENYL T
40 hr at 50°C hydrolysis was nearly complete. The toluene layer was separated, traces of insoluble material were filtered and the solution was cast to form clear but brittle films. The IR spectrum of this polymer is shown in Figure 13, (% calculated for \( C_6F_5SiO_{1.5} : C = 33, F = 43.5; \% \) found: \( C = 32.4, F = 42.2, H = 0.24 \). In this polymer, as in the polymer described in the previous paragraph, traces of hydrogen are mainly due to the presence of hydroxyl end-groups.

F. Ultraviolet and Proton Irradiation

An irradiation facility known as IRIF-I (Ref. 11) was employed in determining the ultraviolet stability (in vacuum) of the polymers synthesized in this study. This instrument, which permits the obtaining of in situ reflectance spectra in the 325- to 2700-nm wavelength region, utilizes A-H6 mercury-argon radiation. Irradiations were carried out at six (6) space acceleration factors. The total doses (ESH) are presented with the data. Silicated zinc oxide was employed as the pigment (Ref. 12). A binder/pigment ratio of 2/1 by weight was used. The data were obtained for clear and pigmented films applied to polished 1/2 x 1" substrates.

The combined radiation facility known as the CREF (Ref. 13) was employed in determining the effect of proton irradiation. The facility is described in Figures 14 and 15. The fluences are presented with the data; the flux employed averaged \( 2 \times 10^9 \) proton/cm\(^2\)-sec.

The IRIF and CREF coupons, which are interchangeable, were prepared by casting the polymer solutions at approximately 3 mils films. The spectral data are recorded in Figures A-1 through A-16 in the Appendix. All samples were irradiated under high vacuum (\(~4.0 \times 10^{-7}\) mm).
Figure 14  COMBINED RADIATION ENVIRONMENT FACILITY

A = Multiple-source adaptor
A' = Beam monitor
B = Fused quartz window
C = Circular first surface mirror
D = Electron port
F = Sweep-collimator lens
G = Isolation valve
H = Einzel lens
J = Faraday cup station
K = Electromagnet
K' = Effective magnetic field
L = Einzel lens
M = Collimator lens
N = RF ion source
V. DISCUSSION

The polydi(pentafluorophenyl)siloxane and the perfluorinated Phenyl T exhibit excellent stability to proton irradiation but are less stable to ultraviolet irradiation. They are even less stable than the analogous unfluorinated polymers in both ultraviolet stability and thermal stability. This was a surprise for us as we expected these perfluorinated structures to be stable. The reason for their instability is not clear, but one can speculate that degradation involves cleavage of the carbon-silicon bonds. In terms of electronegativity, silicon has a value of 1.8 compared with 2.5 for carbon. This results in approximately 12% ionic character for the carbon-silicon bond. The effect of the electronegative pentafluorophenyl group is to withdraw electrons from the carbon atom attached to the silicon. Therefore the ionic character of the C-Si bond is greatly enhanced and the bond becomes reactive (for example it can be attacked by nucleophilic agents). The same effect occurs with an unfluorinated phenyl group attached to the silicon, but is greater with the more electronegative pentafluorophenyl group. The instability of these structures is probably due to the enhanced polarity of the C-Si bond. One can find some analogy with the behavior of the fluoralkyl silicones. The thermal stability of the fluoroalkyl silicones (Ref. 14) depends very markedly on the position of the fluorine relative to silicon:

\[
\gamma \beta \alpha
\]

When fluorine is on the \(\alpha\)-carbon, nucleophilic attack of the C-Si bond is facilitated. This is accompanied by thermal instability. The same effect, to a lesser extent, is observed with fluorine on the \(\beta\)-carbon. High thermal stability and resistance to nucleophilic agents is observed with fluorine on the \(\gamma\)-carbon. This behavior is due to the effect of the electron-attractive fluorine atoms on the polarity of the C-Si

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bond. Also, it has been reported that the tetra(pentafluoro-
phenyl)silane is less thermally stable than tetraphenylsilane
(Ref. 6). One can speculate that the lower stability of the
pentafluorophenylsilanes is due to the inductive effect of the
fluorine atoms present on the phenyl rings.

Although the results of this research did not disprove the
original thesis that perfluoroaromatic polymers would be stable
to the combined charged particle-plus-ultraviolet environment
of deep space, it was shown that perfluorophenylsiloxanes are
not stable to ultraviolet irradiation in vacuum. In summary,
the ultraviolet instability of the perfluorophenylsiloxane
polymers is attributed to the enhanced polarization of the
silicon-carbon bond due to the electron withdrawing effect of
the pentafluorophenyl group. Electron spin resonance studies
that are planned for the future are expected to show that the
Si–C bond is cleaved under ultraviolet irradiation in vacuum.
This behavior is not anticipated for perfluoroaromatic carbon
polymers, such as the perfluorotriazinyl polyethers. Unfortunately,
we were unable to irradiate the completely fluorinated triazinyl
polyethers that we have prepared due to poor film formability or
insolubility in organic solvents.

It is interesting to observe that all the polymers investigated
exhibit excellent stability to proton irradiation. In Figure 16
the effect of proton irradiation on a perfluorinated Phenyl T and
on a 100% methylsiloxane resin (Owens-Illinois 650) are compared.
The somewhat inferior performance of the methylsiloxane resin
tends to support the mechanistic viewpoint that was the genesis
for the research.
Figure 16: EFFECT OF PROTON IRRADIATION IN VACUUM ON THE REFLECTANCE OF PERFLUORINATED PHENYL-T AND OWENS-ILLINOIS 650 RESIN
REFERENCES


Figure A-1: REFLECTANCE OF A TRIAZINYLM POLYETHER OBTAINED FROM HEXAFLUOROBIPHENOL A AND 6-PHENYL 2,4-DICHLOROTRIAZINE BEFORE (---) AND AFTER (--) PROTON IRRADIATION IN VACUUM (1.4 x 10^{15} PROTONS/CM^2)
Figure A-2: REFLECTANCE OF A TRIAZINYL POLYETHER OBTAINED FROM HEXAFLUOROBIPHENOL A AND 6-PHENYL 2,4-DICHLOROTRIAZINE BEFORE (—) AND AFTER (--) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH)
Figure A-3: REFLECTANCE OF A POLYARYLOXYSILOXANE OBTAINED FROM HYDROQUINONE AND DIPHENYL-DICHLOROSILANE BEFORE (--) AND AFTER (—) ULTRAVIOLET IRRADIATION IN VACUUM (1000 ESH)
Figure A-4: REFLECTANCE OF POLYDIPHENYLSILOXANE BEFORE (---) AND AFTER (--) PROTON IRRADIATION IN VACUUM (1.4 x 10^{15} PROTONS/CM²)
Figure A-5: REFLECTANCE OF POLYDIPHENYLSILIOXANE BEFORE (—) AND AFTER (--) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH)
Figure A-6: REFLECTANCE OF PIGMENTED POLYDIPHENYLSILICICATE BEFORE (---) AND AFTER (--) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH)
Figure A-7: REFLECTANCE OF PHENYL T BEFORE (---) AND AFTER (-->) PROTON IRRADIATION IN VACUUM (5.2 x 10^{15} PROTONS/CM^2)
Figure A-8; REFLECTANCE OF PHENYL T BEFORE (—) AND AFTER (--) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH)
Figure A-9: REFLECTANCE OF PIGMENTED PHENYL T BEFORE (—) AND AFTER (—) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH)
Figure A-10: REFLECTANCE OF POLYDI(PENTAFLUOROPHENYL)SILOXANE BEFORE AND AFTER PROTON IRRADIATION IN VACUUM. (—) ORIGINAL; (—...) 1.8 x 10^{15} PROTONS/CM^2; (---) 5.4 x 10^{15} PROTONS/CM^2.
Figure A-11: REFLECTANCE OF POLYDI(PENTAFLUOROPHENYL)SILOXANE BEFORE (---) AND AFTER (--) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH).
Figure A-12: REFLECTANCE OF PIGMENTED POLYDI(PENTAFLUOROPHENYL)SILOXANE BEFORE (--) AND AFTER (—) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH)
Figure A-13: REFLECTANCE OF PERFLUORINATED PHENYL T BEFORE (—) AND AFTER (--) PROTON IRRADIATION IN VACUUM ($5.2 \times 10^{15}$ PROTONS/CM$^2$)
Figure A-14: REFLECTANCE OF PERFLUORINATED PHENYL T BEFORE (---) AND AFTER (--) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESH)
Figure A-15: REFLECTANCE OF PIGMENTED PERFLUORINATED PHENYL T BEFORE (---) AND AFTER (---) ULTRAVIOLET IRRADIATION IN VACUUM (500 ESU)
Figure A-16: REFLECTANCE OF OWENS-ILLINOIS 650 RESIN BEFORE (—) AND AFTER (--) PROTON IRRADIATION IN VACUUM (4.8 x 10^15 PROTONS/CM²)