NASA TECH BRIEF

Marshall Space Flight Center

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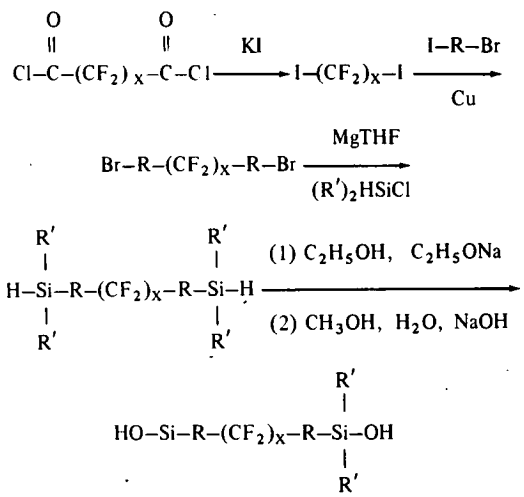
Synthesis of Temperature-and Solvent-Resistant Polymers

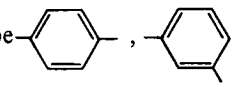
Considerable effort has been put into the search for noncorrosive elastomeric polymers that are solvent resistant and stable at high temperatures. This work has been specifically motivated by the need for a fuel tank sealant in high-speed aircraft, but polymers used as such sealants may also serve as insulation, coatings, or adhesives in other extreme environments.

Silicone polymers, polyimides, and polyisocyanurates offer the greatest potential. Also, it has been found that the incorporation of fluorine atoms in the polymer structure improves the solvent resistance. Some of the most promising developments are presented here.

An elastomeric polysiloxane was synthesized. It showed no degradation after boiling in water, and after a 24-hour soaking in aviation fuel at room temperature, it exhibited a 30% swell in area as compared to 150% for conventional dimethlsilicones. The synthesis is as follows:



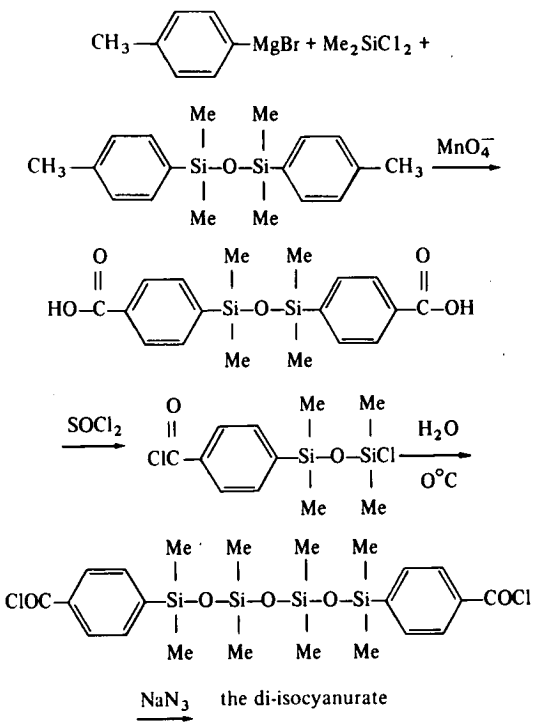
where:

R may be  , and others;

R′ may be an alkyl or phenyl group; and

x may be 3, 4, 6, or 8.

Another approach has been to introduce perfluoro alklyl groups in disilanol chains and polymerize after converting to the isocyanurate. It was found that increasing the siloxane chain, radically improved elastomeric properties. Below is a synthesis of a tetrasiloxane polymer of this kind.



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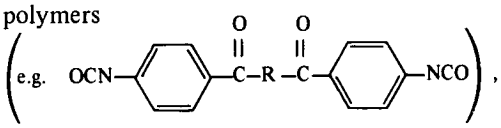
Other synthesis routes were investigated, but the use of $SOCl_2$ in this one is worth noting. Considering the following reported reaction:

$$(Me)_3SiOSiMe_3 \xrightarrow{SOCl_2} 2Me_3SiCl$$

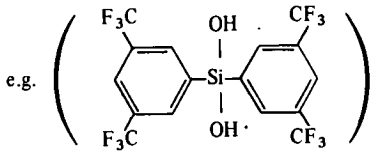
and considering the possibility of silicone-phenyl bond cleavage, the disiloxane acid chloride might not be expected to synthesize as shown. However, the observed reaction is not inconsistent with the stabilizing effect of the para carboxyl groups.

This polyisocyanurate has a tensile strength of 13.8x $10^6 N/m^2$ (2000 psi) with 13% elongation. When boiled 24 hours in aviation fuel at 135°C, the polymer swells slightly with a 30% weight gain.

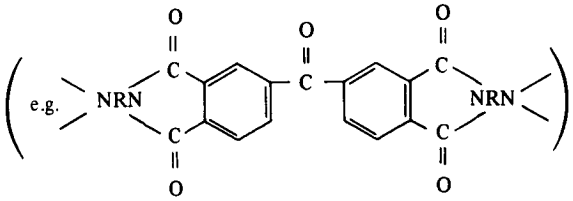
Preliminary work, including synthesis of small amounts of the prepolymer, was done with fluorinated isocyanurate polymers



with fluorinated diol intermediates for incorporation in silphenylene-siloxane polymers



and with modified heterocyclic polyimides



In addition to the compounds and syntheses mentioned here, several others have been tried, and may be of interest to those engaged in polymer research or manufacture.

Note:

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Source: J. A. Webster of
Monsanto Research Corp.
under contract to
Marshall Space Flight Center
(MFS-20848) and,
W. J. Patterson, R. L. Moffett
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