Substituted Silane-Diol Polymers Have Improved Thermal Stability

The problem:
To synthesize a series of organosilicon polymers with improved physical and chemical properties, including stability at elevated temperatures.

The solution:
A series of polymers of the general formula

\[ \text{--OH} \rightarrow \text{Si} \left( \text{R}_2 \text{OR}_4 \right) \rightarrow \text{R} \rightarrow \text{O} \rightarrow \text{n} \]

where \( \text{R} \) represents an aryl group, and \( \text{R}' \) represents an alkyl, aryl-substituted alkyl, biphenyl, or diphenyl ether group.

How it's done:
The experimental work was confined to the polymerization of the stable silylamine, bis (anilino) diphenylsilane, \((\text{C}_6\text{H}_5)_2\text{Si}((\text{NHC}_6\text{H}_5)_2)\), with various diols, including hydroquinone; resorcinol; p,p'-biphenol; 2,7-naphthalenediol; 2,2-propane-bis-(4-hydroxybenzene); 1,6-hexanediol; and 4,4'-dihydroxydiphenyl ether. The silylamine was prepared by reacting diphenyldichlorosilane and aniline. The diols, obtained from commercial sources, were recrystallized before use.

In conducting a polymerization, equimolecular amounts of the silylamine and the selected diol were placed in a thick-walled resin kettle fitted with a heating mantel to facilitate removal of the aniline produced in the reaction, a takeoff condenser, and a vacuum line. A hotplate-magnetic stirrer combination was used for heating and mixing the reactants. Approximately 30 minutes after the reactants were melted, the pressure in the kettle was slowly reduced to approximately 1 mm of Hg, and the reaction was allowed to proceed at a temperature of 300° to 325°C for approximately 6 hours. The polymer produced in the reaction was then removed from the kettle and subjected to various chemical and physical tests.

Of the several polymers that were produced, poly (4,4'-bisoxybiphenylene)diphenylsilane \( \rightarrow \text{Si}((\text{C}_6\text{H}_5)_2) \rightarrow \text{O} \rightarrow \text{C}_6\text{H}_4 \rightarrow \text{C}_6\text{H}_4 \rightarrow \text{O} \rightarrow \text{n} \), formed from bis (anilino) diphenylsilane and p,p'-biphenol, was found to have the most desirable properties. The bulk polymer is a hard, slightly brittle, amber colored solid. It forms a hard protective coating on aluminum, remains stable after being heated at 500°C for 60 minutes, and shows no change after 96 hours at 270°C. The polymer also forms transparent semiflexible films and appears to be suitable for use as an adhesive.

Notes:
1. The application of the poly(4,4'-bisoxybiphenylene) diphenylsilane as a thermal-control coating appears to be especially promising.
2. Inquiries concerning this invention may be directed to:
   Technology Utilization Officer
   Marshall Space Flight Center
   Huntsville, Alabama, 35812
   Reference: B66-10259

Patent status:
Inquiries about obtaining rights for the commercial use of this invention may be made to NASA, Code GP, Washington, D.C. 20546.

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