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THE SYNTHESIS OF ORGANOLYCOXYSILANES AND THEIR CONDENSATION,
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Materials, (No. 8) 13 (1964)

Organoglycoxysilanes have been described before this (1)(2). They have aroused interest in the investigation of their possible condensation reactions and (thus) the opportunity of their incorporation into long chain polymers.

In the present work are described the results of syntheses of trifunctional organoglycoxysilanes by the reaction of ether interchange between methyl-, ethyl- and phenyltriethoxysilane and glycols, their properties and their condensation. The syntheses lead, in excess glycol, to calculation so that by-products of the reaction were removed along with any heterocyclic compounds formed. As shown here, the reaction proceeds in accordance with the equation:



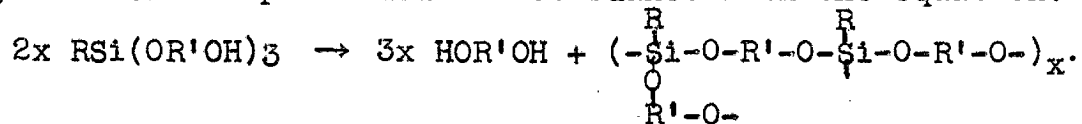
where R = CH₃-, C₂H₅-, C₆H₅-, R' = -CH₂CH₂-, -CH₂CH₂OCH₂CH₂-, -CH₂CH₂CH₂CH₂-.

There was thus obtained a variety of organoglycoxysilanes, as shown in Table 1. A study of the thermomechanical properties of the compounds prepared indicated that their temperatures of brittle point were in the neighborhood of -90° to -70° C. (-130° to -94°F).

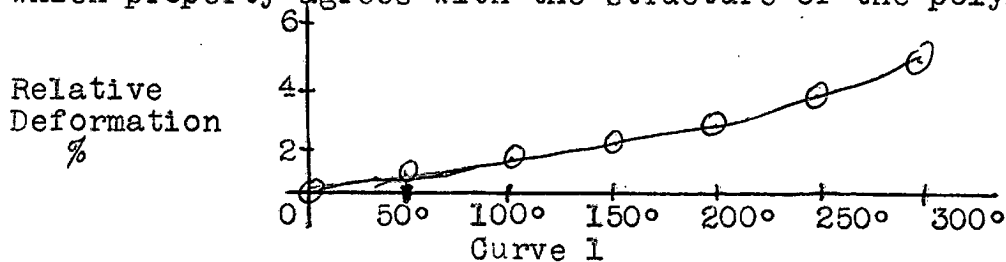
Table 1
(analytical data omitted)

REAGENT	CONC. OF REACTANT		PRODUCT
	GRAMS	MOLS	
Ethylene Glycol	20.351	0.328	Ethyltris-(β-oxyethoxy)-silane
Ethyltriethoxysilane	20	0.104	
Ethylene Glycol	23.75	0.383	Phenyltris-(β-oxyethoxy)-silane
Phenyltriethoxysilane	27.9	0.116	
Diethylene Glycol	25.6	0.25	Ethyltris-(diethyleneglycoxy)-silane
Ethyltriethoxysilane	15.3	0.796	
Diethylene Glycol	27.53	0.259	Phenyltris-(diethyleneglycoxy)-silane
Phenyltriethoxysilane	19.8	0.0824	
1,4-Butane Diol	31.03	0.344	Phenyltris-(γ-oxybutoxy)-silane
Phenyltriethoxysilane	26.3	0.109	

The condensation of pure phenyltris-(δ -oxybutoxy)-silane was carried out under conditions guaranteeing the removal of reaction by-products at 200° C. and 1 mm. In the process of condensation, qualitatively, of the byproducts, there was isolated 1,4-butane diol to the extent of 1.4 mol for each mol of phenyltris-(δ -oxybutoxy)-silane. As in the condensation of methyltris-(diethyleneglyoxy)-silane at 120° C. under 0.025 mm-0.020 mm. there was also diethylene glycol, 1.25 mol for one mol of methyltris-(diethyleneglyoxy)-silane. In each case the reaction was finished after the production of by-product had ceased. The products of condensation were transparent, hard polymers. The polymers prepared from methyltris-(diethyleneglyoxy)-silane were dissolved in alcohol; the polymers from phenyltris-(δ -oxybutoxy)-silane were insoluble in organic solvents. The products formed by these reactions show that polycondensation proceeded in accordance with the equation:

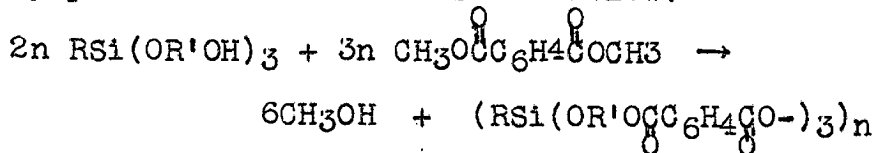


Infrared spectra presented conformed to the chemical structures pertaining to the units of the chain. In the polymers there were observed, often, 1429 cm^{-1} (corresponding to the unit $\text{Si}-\text{C}_6\text{H}_5$) and 3400 cm^{-1} (corresponding to the unit-valence oscillation of the hydroxyl group in the associated state). The thermomechanical properties of the polymers are presented using phenyltris-(δ -oxybutoxy)-silane as shown in Curve 1. As seen, the polymer does not flow up to 300° C., which property agrees with the structure of the polymer.



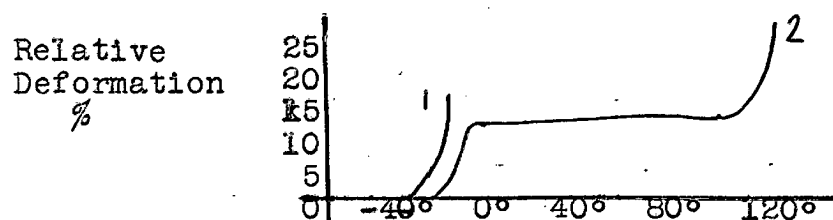
Curve 1
Thermomechanical Properties of the Polymer
Prepared by the Condensation of
Phenyltris-(δ -oxybutoxy)-silane

The condensation of methyl- and phenyltris-(diethyleneglyoxy)-silane with the methyl ester of terephthalic acid took place in equivalent concentrations at 250° C. in the absence of catalyst. In this case the reactions runs easily with production of by-product methanol as shown below:



where $R = \text{CH}_3-$, C_6H_5- ; $R' = -\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$. Methanol was collected in yields of 72% of theory, paralleling the production of polymer which was soluble in a toluene-ethanol mixture.

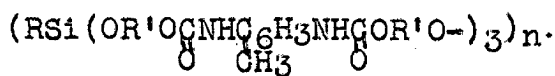
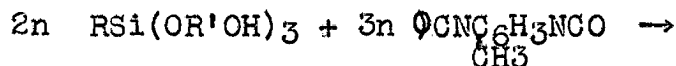
Subsequent condensation produced polymers, insoluble in organic solvents. If the soluble polymers are heated at 200°C . at 1 mm, they pass over to the insoluble polymers. This shows that condensation of methyl- and phenyltris-(diethyleneglycoxy)-silane with dimethyl terephthalate produces a "pro" polymer and that heating rearranges this. The thermomechanical properties of the soluble polymers, prepared from methyltris-(diethyleneglycoxy)-silane and dimethyl terephthalate and the properties of the polymers after supplementary condensation at 250°C . and heating two hours are shown in Curve 2. In the condensation of the oxysilane with dimethyl terephthalate no further production of glycol was observed as with the condensation of the original organoglyoxysilane.



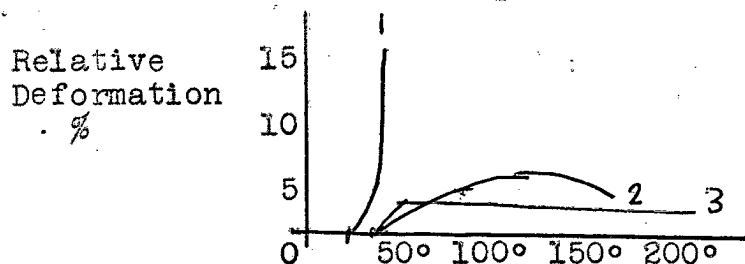
Curve 2

Thermomechanical Properties of the Polymers Produced from Methyltris-(diethyleneglycoxy)-silane and Dimethyl Terephthalate. 1- as formed, 2-after heat treatment.

The condensation synthesis of organoglycoxysilanes with tolylene diisocyanate produced cyclic polymers as shown below:

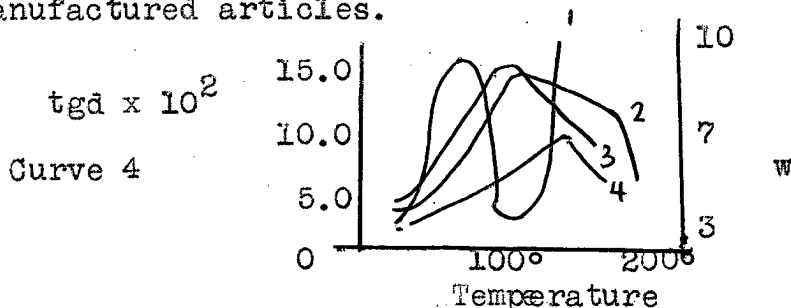


In the reactions as run, the effect of heat was noticed, the amount of which depended on the numerical amounts of the reactants. The thermomechanical properties of the polymers are shown in Curve 3, from which it is seen that the polymers are liquids at 30° - 40°C ., that after six hour treatment at 150°C . the liquids have practically disappeared, and that it shows that these are the final possible structures of the polymers.



Curve 3. Thermomechanical Properties, of Polymers:
 1. Prepared from Ethyltris-(β -oxyethoxy)-silane and Toluene Diisocyanate as Formed. 2. Same, after Heating. 3. Prepared from Phenyltris-(diethyleneglyoxy)-silane and Toluene Diisocyanate after Heating.

From these polymers one can prepare many different manufactured articles.



Dielectric characteristics of the polymers prepared from phenyltris-(β -oxybutoxy)-silane and toluene diisocyanate. Tangent angle of dielectric loss: 1. at $f = 400$ gts. 2. $f = 1.5 \times 10^6$ gts. Dielectric permeability: 3. at $f = 400$ gts. 4. at $f = 1.5 \times 10^6$ gts.

An investigation of the electrical properties of typical polymers classified as plastics shows a sharp maximum dependence of dielectric loss on temperature. The Debaevskii maximum (Curve 4) at the point 400 gts lies at 78°C ; at the point 1.5×10^6 it is shifted to one side at the higher temperature of 125°C .

Each property of these polymers was investigated.

Table 2
 (analytical data omitted)

Compound	n_D^{20}	d_4^{20}
$\text{CH}_3\text{Si}(\text{OCH}_2\text{CH}_2\text{OH})_3$	1.4515	1.1980
$\text{C}_2\text{H}_5\text{Si}(\text{OCH}_2\text{CH}_2\text{OH})_3$	1.4538	1.1642
$\text{C}_6\text{H}_5\text{Si}(\text{OCH}_2\text{CH}_2\text{OH})_3$	1.5025	1.2068
$\text{C}_2\text{H}_5\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})_3$	1.4588	1.1478
$\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})_3$	1.4969	1.1862
$\text{C}_6\text{H}_5\text{Si}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$	1.4967	1.1115

Experimental Part

For the reactions of esterification (we) took pure alkyl (aryl)triethoxysilane and dry glycol.

Preparation of Methyltris-(β -oxyethoxy)-silane. In a flask were placed 21.01 g. (0.34 mol) of ethylene glycol and through a dropping funnel there was introduced with heating and intensive stirring, 20.1 g. (0.113 mol) of methyltriethoxysilane. There was formed at first an emulsion with distillation of by-product alcohol. The temperature was maintained for four hours at 175° C. After this, 13.15 g. of alcohol had been collected (85.2% of theory). The main product of the reaction was vacuum distilled at 5 mm. and 100°-120° C.

The product of the reaction was a viscous colorless liquid, n_D^{20} 1.4515, d_4^{20} 1.1980. MR 50.96; calculated MR 51.168.

Analysis, Found % OH 22.16, 22.73; Si 12.95, 12.65; Mol. Wt. 227. $C_7H_{18}O_6Si$

Calculated, %; OH 22.5; Si 12.4; Mol. Wt. 226.3°

By similar methods (the other) organoglyoxysilanes were synthesized and identified (Table 2).

Condensation of Phenyltris-(δ -oxybutoxy)-silane. 12.1 g. (0.0325 mol) of phenyltris-(δ -oxybutoxy)-silane was condensed by heating two hours at a temperature of 200° C. in a vacuum of 2 mm. The yield was 4.02 g. (0.0446 mol) of 1,4-butanediol, n_D^{20} 1.4458, d_4^{20} 1.0105, m.r. 23.76; calculated 23.6g

The product of the reaction, a transparent, light-yellow hard polymer, was insoluble in most organic solvents.

Condensation of Methyltris-(diethyleneglycoxy)-silane and the Dimethyl Ester of Terephthalic Acid. In a reaction flask, 8.4 g. (0.023 mol) of methyltris-(diethyleneglycoxy)-silane and 6.82 g. (0.0422 mol) of dimethyl terephthalate were mixed and the reaction mass stirred at 250° C. for one hour. The yield was 1.46 g. (0.0456 mol) of methanol (72% of theory) and a reaction mass of yellow-brown material (which was) heated to fusion. A test of its solubility showed that the product of the reaction was soluble in a mixture of alcohol and toluene. Subsequent vacuum distillation of the reaction product for two hours at 150°-200° C. and 2 mm. brought out the desired polymer, insoluble in organic solvents.

Condensation of Phenyltris-(diethyleneglycoxy)-silane and Dimethyl Terephthalate. This was accomplished by a method analogous to the above. For the condensation, 5.85 g. (0.0139 mol) of phenyltris-(diethyleneglycoxy)-silane and 4.05 g. (0.0244 mol) of dimethyl terephthalate were taken, yield 0.8 g. (0.025 mol) of methanol (60% of theory).

The product of the reaction was a light yellow, hard polymer.
Condensation of Methyltris-(β -oxyethoxy)-silane with Toluene Diisocyanate. There were mixed 1.16 g (0.0051 mol) of methyltris-(β -oxyethoxy)-silane and 1.2 g. (0.007 mol) of toluene diisocyanate; then the temperature was raised from 18° to 40° C. At the beginning the mixture formed an emulsion which disappeared after five minutes. The transparent liquid mass was poured out onto a plate and left to harden by drying at room temperature for 20 hours, then placed in an oven and dried for six hours at 150° C. The reaction product was a hard transparent polymer.

Found, %: N 9.18, 9.16. Calculated, %: N 8.62.

The condensations of other (related) organoglycoxysilanes with toluene diisocyanate were carried out by the same method (Table 3).

Table 3

Characteristics of Organoglycoxysilanes, Condensed with
 Toluene Diisocyanate
 (analytical data omitted)

Initial Reactants	Amount Taken for the Reaction	
	g	mol
Ethyltris-(β -oxyethoxy)-silane	1.07	0.0045
Toluene Diisocyanate	1.28	0.0074
Phenyltris-(β -oxyethoxy)-silane	1.07	0.0037
Toluene Diisocyanate	1.02	0.006
Ethyltris-(diethyleneglycoxy)-silane	1.13	0.003
Toluene Diisocyanate	0.84	0.0048
Phenyltris-(diethyleneglycoxy)-silane	1.18	0.0028
Toluene Diisocyanate	0.77	0.0044
Phenyltris-(β -oxybutoxy)-silane	1.17	0.0031
Toluene Diisocyanate	0.86	0.0049

Summary

1. The reaction of methyl-, ethyl- and phenyltriethoxysilane with glycols serves to synthesize the following: methyl-, ethyl- and phenyltris-(β -oxyethoxy)-silane, ethyl- and phenyltris-(diethyleneglycoxy)-silane and phenyltris-(δ -oxybutoxy)-silane from which were prepared polycondensation products (polymers).

2. The condensation of synthetic organoglycoxysilanes with the dimethyl ester of terephthalic acid, (with) tolylene diisocyanate serve as the source of other polymers.

Literature

1. M.M. Sprung, J. Org. Chem., 23 (No. 1) 58 (1958)
2. Sb. Heteroliner High Molecular (Weight) Compounds, "Science", 18 (1964)

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