

Silane Polysulfide Polymers as Solid Composite Propellant Binders

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Synopsis

Two mercaptosilane monomers were prepared and polymerized by oxidation to yield mercaptan functional silane polysulfide polymers. The mercaptosilane monomers were of the general formula, $[\text{HS}(\text{CH}_2)_x]_2\text{SiY}_2$, where $x = 3$ and $\text{Y} = \text{Et}$ or Me . These monomers were prepared by the addition of thiolacetic to diallyldialkylsilanes. The dithiolacetate that resulted from the addition reaction was hydrolyzed in alcoholic NaOH yielding the dimercaptan. Polymerization of the dimercaptan was accomplished with peroxides, iodine, or sulfur, yielding polymers of a molecular weight of approximately 1200. These polymers were cured to solid elastomers with mild oxidizing agents. The mercaptan monomers were also redistributed with diethylformal polysulfide polymers, which were then cured to solid elastomers with mild oxidizing agents. The redistributed silane-diethylformal polymers were used to make composite solid propellants. A 50% increase in propellant burning rate and a 16°C . lowering of the glass transition temperature were found when the redistributed polymer was used in place of diethylformal polymers as a propellant binder. Experimental procedures are given.

INTRODUCTION

Since the advent of composite solid propellants, propellant chemists have made many attempts to improve the physical properties and to tailor the burning rates of these fuels. This paper describes one of these attempts—a successful attempt that has not been published until now because of security considerations.

In their simplest form, composite solid propellants consist of an oxidizer, normally an inorganic compound, that is dispersed in a rubbery fuel-binder, normally an elastomeric organic matrix. Although, as with all filled elastomers, the physical properties of solid propellants depend to some extent on the particle size and the particle size distribution of the solid filler, the properties of the propellant are much more dependent upon the physical properties of the elastomeric fuel binder. Thus, a major improvement in the physical properties of propellant requires a major change in the physical properties of the fuel-binder. Conversely, the burning rate of the propellant, to a large extent, is determined by the particle size and particle

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size distribution of the oxidizer. The binder composition does, however, have some influence on burning rate. Hence, a change in the fuel-binder can be expected to influence the physical properties and the burning rate of a propellant, but in varied degrees.

In the early 1950's, Thiokol Chemical Corporation was using its polysulfide polymers as the binder for its solid propellants. These polymers gave the propellants excellent physical properties and inherent resistance to the deleterious effects of atmospheric oxygen, ozone, atmospheric moisture, and high and low temperatures. For the more usual commercial applications, the low-temperature physical properties of Thiokol polysulfide polymers were entirely sufficient. However, for their use in solid propellants, there was some room for improvement. There was a need to extend the low temperature capability of the polysulfide propellant to below its -51°C . limit.

This need led to the program described in this article, a program in which the excellent general characteristics of the polysulfide propellants were combined with the very promising low temperature characteristics of the silanes.

Because of the low fuel value of the siloxane structure ($\text{Si}-\text{O}-\text{Si}$), this program was pointed toward the possibility of forming a silane ($-\text{C}-\text{Si}-\text{C}-$) polysulfide polymer. This approach was a result of the belief that the desired low temperature performance could be attained by introduction of a heteroatom in the backbone of the carbon chain to decrease crystallinity and interchain forces.

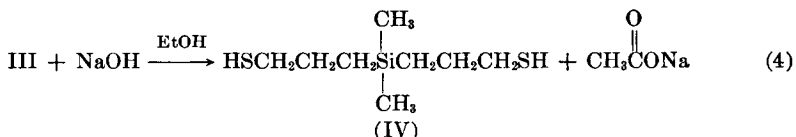
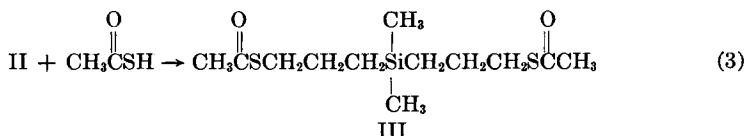
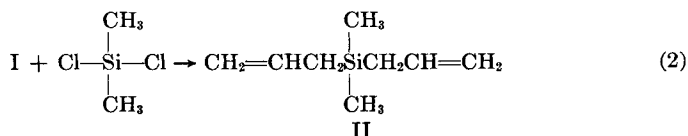
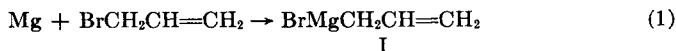
One other known characteristic of the silicon atom lead us to a choice of silane polysulfides as binders for solid propellants. It was known that certain elements would alter the burning rate of composite solid propellant. Silicon was among these elements. Thus, through one atom, we hoped to improve low-temperature physical properties and modify propellant burning rate.

MONOMER PREPARATION

Marvel and Cripps¹ prepared mercaptan-containing silanes which might be oxidized to polysulfide polymers, which, in turn, might be compatible with the commercial polysulfides. This general preparation method was used for the preparation of the silane monomers. Dimethyl bis(3-mercaptopropyl)silane was prepared by reacting dimethyldiallylsilane with thiolacetic acid, followed by hydrolysis of the dithiolacetate with base to give the dimercaptan.

Because the diallyl compound was not commercially available in the early part of this work, it was synthesized by means of Grignard reactions involving allylmagnesium bromide and dimethyldichlorosilane. Allyl bromide gave much better yield than did allyl chloride, and the yield was increased even further by using a large excess of the Grignard reagent. Hydroquinone was used, in a few instances to inhibit vinyl polymerization

during the distillation of the diallylsilane, but its use did not increase the yields and the hydroquinone codistilled with the product making purification difficult. Its use was discontinued. Soon after the work was started, small quantities of dimethyldiallylsilane became commercially available, and this preparation was discontinued. Before this occurred, several batches were made in very large quantities, and the yield of the diallylsilane was raised to 82%. This series of reactions is shown in eqs. (1)–(4).



Because the effect of the length of the side group on the silicon atom was not known, the synthesis of diethyl bis(3-mercaptopropyl)silane was carried out, along with synthesis of the dimethyl compound. Synthesis of the diethyl compound involved the preparation of the intermediate, diethyldiallylsilane. The general preparative procedure for this material was identical to that used for the dimethyl compound.

Preparation of the dimercaptan from the diallylsilane was carried out according to the method of Marvel.¹ Essentially, this preparation involves the addition of thioacetic acid to the diallyl compound in cyclohexane, and then hydrolyzing the resulting dithiolacetate to the dithiol. The yield of the dimercaptan could be increased by using a 50% excess of the acid. Excess acid and cyclohexane were removed by distillation and were recycled into another reaction. Distillation was used in the early experiments to isolate the crude dithiolacetate formed in the addition reaction. It soon became evident that the distillation did not materially improve the quality of the product and some product losses were encountered because of this step. In addition, tar formation took place during the distillation because of the very high boiling point of the dithiolacetate. Later, it was found that hydrolysis of the dithiolacetate to the corresponding dithiol could be accomplished without going through the intermediate step of isolating the dithiolacetate. Hydrolysis was accomplished in two ways: (1) the use of an alcohol–water solution of sodium hydroxide and (2) the use of a large

excess of methanol in the presence of a trace of base. The first procedure was the more successful when the reactions were run on a large scale. It did not, however, give complete hydrolysis in one step, despite the fact that 100% excess base and long heating periods were used. The infrared spectrum of the product of the first hydrolysis always showed some absorption due to the carbonyl group. Consequently, a second hydrolysis was always required to remove the last traces of ester. This second hydrolysis was carried out at a ratio of 8 moles of partially hydrolyzed dithiolacetate to 1 mole sodium hydroxide.

The same general procedure was used for making the diethyl bis(3-mercaptopropyl)silane.

Because the monomers prepared by the above procedures were not entirely mercaptan-terminated, i.e., their functionalities were below 2, it was necessary to use a trifunctional mercaptan in the polymerizations to obtain high molecular weight polymers. One of the simplest trimercaptans is 1,2,3-propanetrithiol. Two synthetic methods were examined for its preparation. One² called for the reaction of 1,2,3-trihalopropane with sodium hydrogen sulfide, and the other,³ the reaction of the same trihalide with sodium thiolacetate. In the first reaction, the yields of distilled 1,2,3-propanetrithiol were in the range of 5% to 10%. Final purification of the compound was difficult and the quality of the product varied drastically from batch to batch. Although the second reaction was somewhat smoother, hydrolysis of the ester to the trimercaptan was never completely successful. Because of these difficulties, methyl tris(3-mercaptopropyl)silane was prepared. The procedure used was the same as that for the preparation of the dimercaptosilanes, except that the starting material was methyltrichlorosilane rather than dimethyldichlorosilane. The product was obtained in 56% yield and the functionality, as measured by endgroup titration, was approximately 2.75.

After initially performing a carbon, hydrogen, and silicon analysis on each of the products made, infrared spectra and boiling points were used for quality control. An absorption peak at about 1600 cm.^{-1} in the spectrum of the diallylsilane disappeared after the diallyl compound was reacted with thiolacetic acid, and an absorption peak at 1725 cm.^{-1} in the spectrum of dimethyl bis(3-mercaptopropyl)silane diacetate vanished during the hydrolysis of the diacetate to the dimercaptan. This latter absorption peak was especially helpful in determining when the hydrolysis of the dithiolacetate was complete. These two frequencies were assigned as terminal carbon-carbon unsaturation and carbonyl, respectively.

POLYMER PREPARATION

Polymerization of the silane mercaptans was carried out with a number of oxidizing agents: hydrogen peroxide, peracetic acid, iodine, and sulfur.

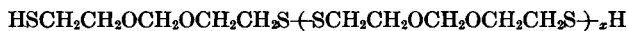
Hydrogen peroxide, used in conjunction with a trace of base, caused an exothermic reaction, but the resulting polymer had a low molecular weight

and its terminals were not oxidizable to give a higher molecular weight, i.e., these polymers did not cure to a rubbery state. When the amount of base was increased to the stoichiometric quantity, a polymer of higher molecular weight was obtained; however, it was not entirely functionally terminated and, again, a cured disulfide polymer could not be formed. Oxidation with peracetic acid gave results similar to those obtained with hydrogen peroxide.

An aqueous solution of iodine and potassium iodide was used to polymerize a solution of diethyl bis(3-mercaptopropyl)silane made by dissolving the mercaptan in water with an equivalent amount of KOH. A 30% excess, of the stoichiometric amount, of the iodine-potassium iodide solution polymerized the monomer to a molecular weight of only 1300-1500. This polymer was contaminated with iodine and various salts, and its purification was complicated by emulsification with water. The emulsification problem was resolved by first adding acid and then benzene, and azeotroping the water from the emulsion. Excess iodine was removed by treating a dried benzene solution of the polymer with sodium thiosulfate. After this treatment, the benzene was evaporated, and a light yellow polymer remained. Since the polymer had a functionality of less than 2, complete curing of the silane polysulfide by oxidizing agents, such as TNT, *p*-quinone dioxime, or lead peroxide, was prevented. Some crude rubbers were obtained from reactions in which a crosslinking agent was added. About one pound of polymer was prepared using iodine as the oxidizing agent.

The most successful polymerizations were run with the use of sulfur as the oxidizing agent. Since the sulfur was soluble in the monomer, the reactions could be run in bulk without solvent, and the reaction mixture was homogeneous. This oxidation reaction proceeds best under basic conditions and triethylamine was found to be an efficient catalyst. When the stoichiometric quantity of oxidant was used, the polymers consistently had a molecular weight of 1200. Hydrogen sulfide produced in the reaction boiled out and the last traces of it were removed under reduced pressure. This procedure was used successfully for batches up to 5 lb. In some of the earlier batches of polymer containing crosslinking and using 120% of the stoichiometric amount of sulfur, polymerization continued at a low rate after the initial reaction, and a soft rubber was formed in a period of 6 weeks at room temperature.

In order to extend the quantity of the silane mercaptans, so as to obtain more information concerning physical and ballistic properties of propellant made from the polymer, blends were made with one of Thiokol's polysulfide polymers. These polymers, identified by the initials LP followed by a number, are dialkylformal polysulfides. The particular ones used for this series of experiments are diethyl formal polysulfides that have the structure:



When heated at only moderately high temperatures, about 70°C., the various polysulfide polymers will redistribute their molecular segments, thus forming a uniform product from a mixture.⁴ This process of redistribution was used as a means of obtaining a new polymer for testing as a solid propellant binder. Various quantities of LP-2 and LP-32 were blended with the silane mercaptan monomers. These blends were heated for 72 hr. at 70°C. to bring about redistribution among the two distinct molecular species. The average molecular weight and final viscosity of the polymers formed by this means were dependent upon the ratio of silane monomer to LP. In those cases where the viscosity and molecular weights were low, the redistributed polymer was oxidized with sulfur to a molecular weight of about 1200. All of the silane polysulfides made by redistribution required the addition of some trifunctional mercaptan before they could be cured to rubbery stocks. The amount of crosslinking required for optimum physical properties was determined experimentally. These redistributed copolymers of the mercaptosilanes and the diethylformal polysulfide polymers were identified by letters and numbers. A tabulation of the composition of four of these redistributed polymers is shown in Table I.

TABLE I

| Silane polysulfide | Wt. DMDMPS, g. ^a | Wt. DEDMPS, g. ^b | Wt. LP-2, g. ^c | Wt. LP-32, g. ^d | MTMPS, mole-% ^e |
|--------------------|-----------------------------|-----------------------------|---------------------------|----------------------------|----------------------------|
| SPS-3 | 60 | | 40 | | 2.0 |
| SPS-4 | | 60 | 40 | | 2.0 |
| SPS-5 | 20 | | | 80 | 0.5 |
| SPS-6 | | 20 | 80 | | 2.0 |

^a DMDMPS = dimethyl bis(3-mercaptopropyl)silane.

^b DEDMPS = diethyl bis(3-mercaptopropyl)silane.

^c LP-2 = diethylformal polysulfide polymer, molecular weight about 4000, 2% cross-linked.

^d LP-32 = diethylformal polysulfide polymer, molecular weight about 4000, 0.5% cross-linked.

^e MTMPS = methyl tris(3-mercaptopropyl)silane; mole-% based on DMDMPS or DEDMPS.

POLYMER EVALUATION

A typical polysulfide-ammonium perchlorate propellant formulation was selected and its physical and ballistic properties used for comparison with the propellants made of the silane polymers. The quantities of oxidizer, fuel, additives, and other propellant ingredients were not altered. All propellants were mixed with the use of standard composite solid propellant processing equipment and were considered processable, but the viscosity at the end of mixing time was slightly higher for those propellants containing silicon than for those with the LP polymer.

Small rocket motors, containing about 3 lb. of propellant were made and tested over the pressure range of 800–2600 psia. The results of the testing of these motors are shown on Figures 1 and 2. These burning rate data are summarized in Table II, along with the measured physical property data for the propellants. A sizable increase in propellant burning rate

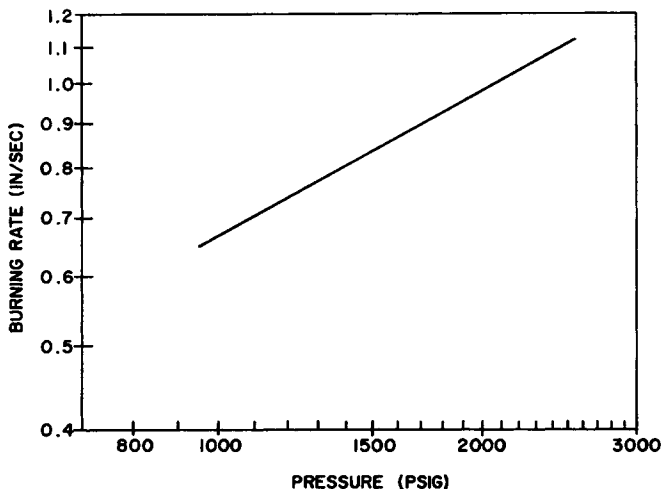


Fig. 1. Burning rate vs. pressure for propellant made with SPS-5 polymer.

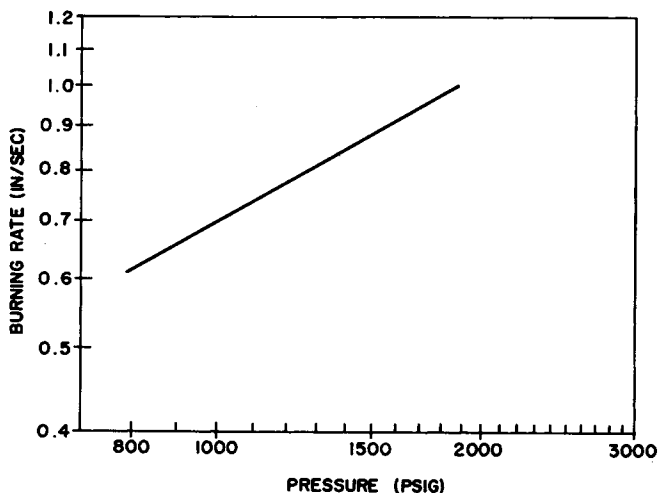


Fig. 2. Burning rate vs. pressure for propellant made with SPS-6 polymer.

was achieved by incorporating silicon into the polymer backbone. It appears that the amount of the silicon in the polymer did not have a critical affect on propellant burning rate. This is evident, from the fact that propellant made with SPS-3 polymer, which contained 8.1% silicon, burned at a rate of 0.7 in./sec. at 1000 psia, while propellant made from SPS-5

polymer, which contained 2.14% silicon, burned at 0.68 in./sec. at the same pressure.

Several motors were tested at very low temperatures, -62 , -67 , and -73°C . Those motors tested at -62°C . were all successful, about one-half of the motors tested at -67°C . were successful, and all of the motors tested at -73°C . blew up. The motor malfunctions were caused by the propellant grain breaking or cracking at the low temperature, which caused an increase in the propellant burning surface. This increased burning surface caused excessive pressure buildup within the rocket motor, and the motor case burst.

TABLE II
Properties of the Various Silane Polysulfide Propellants

| | Polymer type | | | |
|---|--------------------------|-----------|------------|-------------|
| | Base formulation (LP-33) | I (SPS-3) | II (SPS-5) | III (SPS-6) |
| Burning rate at 1000 psia, in./sec. | 0.46 | 0.70 | 0.68 | 0.70 |
| Increase over base formulation in burning rate, % | — | 52 | 48 | 52 |
| c^* , ft./sec. ^a | 4410 | 4662 | 4511 | 4371 |
| Modulus at 27°C ., psi | 2100 | 575 | 875 | 1000 |
| Maximum stress at 27°C ., psi | 188 | 87 | 240 | 175 |
| Maximum strain at 27°C ., % | 25 | 41 | 69 | 43 |

^a c^* is an indication of the usable energy of a propellant and is defined, mathematically, as $c^* = P_c A_T g / \dot{w}$, where P_c is the rocket motor chamber pressure, A_T is the area of the rocket motor throat, g is the gravitation constant, and \dot{w} is the weight rate of flow of the propellant combustion gases from the rocket motor.

Physical properties of each of the propellants shown in Table II were measured over the temperature range of -77 to 60°C . on an Instron tensile tester. Plots of the tensile properties of the propellant made with SPS-5 and SPS-6 polymers are shown on Figure 3. The brittle point of the propellants made from SPS-3, SPS-5, and SPS-6 all lay in the region of -67°C . Glass transition temperature measurements of a polymer made from dimethyl bis(3-mercaptopropyl)silane with methyl tris(3-mercaptopropyl)silane as the crosslinking agent showed this point to be -68°C . For SPS-3, a 60/40 blend of the dimethylmercaptosilane and LP-2, the glass transition temperature was -65°C .

The motor test data were confirmed by the results of the physical property testing of the propellant and indicated that the low temperature firing limit of the propellant was based upon the polymer's glass transition

temperature. In the case of the silane polysulfides, this temperature is about -67°C .

As a further test of the physical properties of the silane polymers, their long-term high-temperature aging characteristics were measured. Several

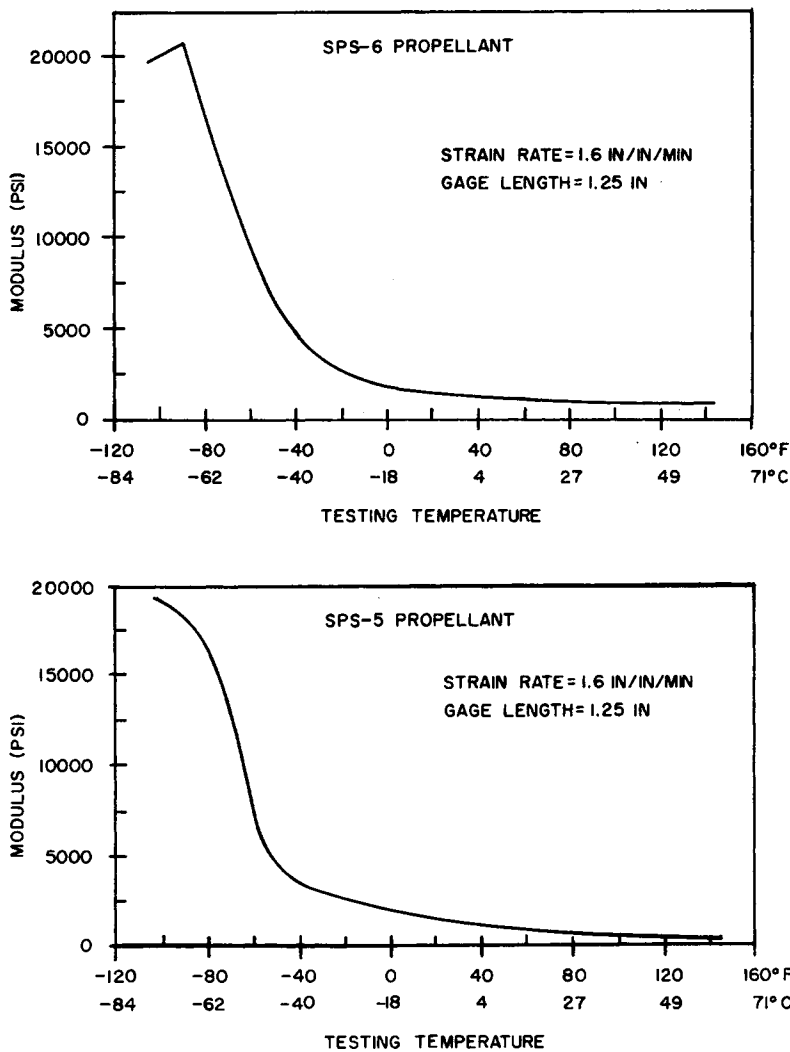


Fig. 3. Relationships of modulus and temperature for two silane polysulfide polymers.

samples of propellant made from SPS-3 were stored at 76°C . for 24 weeks. There was a small increase in modulus during the first week of storage due to additional cure of the SPS-3 binder. After that time, however, there was no change in modulus, and the appearance of the aged propellant was similar to that of unaged propellant.

EXPERIMENTAL

Preparation of Diethyldiallylsilane

A 22-liter flask was fitted with a 1-liter dropping funnel, a mechanical stirrer, and two large reflux condensers cooled with circulating ice water. Drying tubes were attached to the top of the condensers and the dropping funnel. The flask was charged with magnesium turnings (480 g., 20 mole) and heated, in an atmosphere of nitrogen, to remove water. Sufficient sodium-dried ether was added to cover the magnesium turnings and the reaction started by adding 10 ml. of allyl bromide. Allyl bromide (242 g., 2 mole) was then added dropwise at a rate that maintained a vigorous but controlled reaction. After this addition was complete, an ether (2 liters) solution of diethyldichlorosilane (942 g., 6 mole) and allyl bromide (1452 g., 12 mole) was added dropwise over a 4-hr. period. To assure complete reaction of the chlorosilane, a final addition of allyl bromide (242 g., 2 mole) and ether (the amount varied, depending upon the amount needed to maintain fluidity of the mixture in the reaction vessel) was made. The reaction was stirred an additional 3 hr., then a 5-liter portion of water was added slowly to hydrolyze the excess Grignard reagent. Finally 1 liter of hydrochloric acid was added to destroy unreacted magnesium. When hydrolysis was complete, the ether layer was separated and the water layer extracted twice with 1.5-liter quantities of ether. The ether layer and extracts were combined and dried first over calcium chloride and then over sodium sulfate. This ether solution was distilled first under reduced pressure to remove the ether and then at a low pressure to obtain the product. A total of 835 g. of product (82% yield) was obtained; b.p. 70.5–71.0°C./16 mm., n_D^{29} 1.4565, d_4^{29} 0.7962.

ANAL. Calcd. for $C_{10}H_{20}Si$: C, 71.4%; H, 11.9%. Found: C, 70.55%; H, 11.55%.

Preparation of Dimethyldiallylsilane

The procedure and molar quantities used were identical to that used to prepare diethyldiallylsilane, except that dimethyldichlorosilane was used in place of diethyldichlorosilane. The product, obtained in 70% yield, boiled at 51–57°C./37 mm., n_D^{25} 1.4374, d_4^{29} 0.9257.

Preparation of Methyltriallylsilane

The same general procedure used for dimethyldiallylsilane was employed. The relative amounts of reagents used were 1 mole of methyltrichlorosilane, 4 mole of allyl bromide, and 5 mole of magnesium. The product boiled at 65–67°C./15 mm. and was obtained in 56.5% yield; d_4^{29} 0.973, n_D^{25} 1.4638.

ANAL. Calcd. for $C_{10}H_{18}Si$: C, 72.3%; H, 10.8%; Si, 16.9%. Found: C, 71.68%; H, 10.44%.

Preparation of Dimethyl Bis(3-mercaptopropyl)silane (DMDMPS)

Dimethyldiallylsilane (560 g., 4 mole) was placed in a 5-liter three-necked flask fitted with a mechanical stirrer, dropping funnel, and a reflux condenser. A solution of thiolacetic acid (912 g., 12 mole) in 1000 ml. of purified cyclohexane was added dropwise at such a rate that gentle reflux occurred. The reaction was refluxed and stirred for three hours after this addition was complete. Excess thiolacetic acid was then distilled from the mixture, distillation being discontinued when the pot temperature reached 145°C. The residue was then transferred to a 5-liter three-necked flask containing sodium hydroxide (400 g., 10 mole) dissolved in water (1500 ml.) and ethanol (500 ml.). After the initial reaction subsided, the mixture was refluxed for 4 hr. and then acidified with acetic acid. The dimercaptan separated and was taken up in benzene, the water layer extracted three times with 500-ml. portions of benzene, and the benzene extracts combined. The benzene was distilled from the mixture and the product distilled under reduced pressure. The infrared spectra of the distillate invariably showed absorption in the carbonyl region, so the distillate was rehydrolyzed. This second hydrolysis was carried out with sodium hydroxide (20 g., 0.5 mole), water (375 ml.), and alcohol (125 ml.) by the same method used in the first hydrolysis. That material distilling at 100–110°C./150 μ was taken as the product (738 g., 88.5%) n_D^{15} 1.5043, d^{20} 0.9523, viscosity 4.6 cp.

Preparation of Diethyl Bis(3-mercaptopropyl)silane (DEDMPS)

This procedure and molar ratios were identical to that used for the preparation of dimethyl bis(3-mercaptopropyl)silane, except that diethyldiallylsilane was used in place of the dimethyldiallylsilane. The product had b.p. 100–110°C./70 μ , n_D^{25} 1.5074, d^{20} 0.9578, viscosity 4.8 cp.

ANAL. Calcd. for $C_{10}H_{24}S_2Si$: C, 50.8%; H, 10.0%; S, 27.2%. Found: C, 50.07%; H, 9.53%; S, 26.61%.

Preparation of Methyl Tris(3-mercaptopropyl)silane (MTMPS)

The general procedure was the same as that used for the preparation of dimethyl bis(3-mercaptopropyl)silane with a few modifications. A 4-mole portion of thiolacetic acid was used with 0.565 mole of methyltriallylsilane. The final product was not distilled, since all attempts to distil it resulted in decomposition. The yield was 94.5%.

ANAL. Calcd. for $C_{10}H_{24}S_3Si$: S, 35.8%. Found: S, 33.05, 32.85%.

Hydrogen Peroxide Polymerization of Diethyl Bis(3-mercaptopropyl)silane

A solution of diethyl bis(3-mercaptopropyl) silane (10 g., 0.043 mole) in 10 ml. of 10% aqueous sodium hydroxide was cooled to 10°C. with an ice bath. Hydrogen peroxide (5.3 g., 0.047 mole) was then added at such a

rate that the temperature remained below 15°C. After the addition, the solution was stirred an additional 15 min. and then acidified with acetic acid. The polymer was then extracted from the water with ether. The ether extract was dried over sodium sulfate, filtered, and the ether removed under reduced pressure, leaving a lemon-colored polymer having a molecular weight of 1100.

The use of peracetic acid gave a polymer of about the same molecular weight.

Iodine Polymerization of Diethyl Bis(3-mercaptopropyl)silane

A solution of iodine (254 g., 1 mole) and potassium iodide (322 g., 2 mole) in 800 ml. of water was added dropwise at 70°C. to a solution of diethyl bis(3-mercaptopropyl)silane (236 g., 1 mole), 1,2,3-trimercaptopropane (7 g., 3% based on the dimercaptan), and potassium hydroxide (112 g., 2 mole) in 600 ml. of water. After the reaction mixture became colorless, the water was decanted and the residual polymer dissolved in benzene. This benzene layer became emulsified with water, and hydrochloric acid was added to break the emulsion. The milky benzene layer was separated and dried by azeotroping the water from the mixture with benzene. This dried polymer solution was shaken with solid sodium thiosulfate to remove unreacted iodine, then filtered. The benzene was removed under reduced pressure, leaving a clear, lemon-colored polymer; molecular weight (ebullioscopic) 1500; molecular weight (endgroup titration) 1600; viscosity (Brookfield) 42.4 poise; viscosity (McMichael) 42.6 poise; density 1.045; mercaptan, 3.0%.

Sulfur Polymerization of Dimethyl Bis(3-mercaptopropyl)silane

Into a 100-ml., three-necked flask equipped with a mechanical stirrer were placed dimethyl bis(3-mercaptopropyl)silane (10.4 g., 0.05 mole), triethylamine (0.21 g., 2% of the monomer), and methyl tris(3-mercaptopropyl)silane (0.52 g., 5% of the monomer). The flask was placed in an oil bath preheated to 75°C. Sulfur (1.94 g., 0.061 mole) was added slowly with stirring. At the end of the reaction, the mixture was heated and stirred for 10 min. more. Dissolved H₂S and triethylamine were removed under reduced pressure leaving a light greenish-gray polymer with a molecular weight of about 1100.

Sulfur Polymerization of Diethyl Bis(3-mercaptopropyl)silane

Diethyl bis(3-mercaptopropyl)silane (11.8 g., 0.05 mole), methyl tris(3-mercaptopropyl)silane (0.83 g., 7% by weight of the monomer), and triethylamine (0.24 g., 2% by weight of the monomer) were placed in a flask and heated to 75°C. Then sulfur (2.14 g., 0.067 mole) was added with stirring. The remainder of the procedure was identical to that used for the sulfur polymerization of dimethyl bis(3-mercaptopropyl)silane.

Preparation of SPS-3

Dimethyl bis(3-mercaptopropyl)silane (1362 g.), LP-2 (908 g.), and methyl tris(3-mercaptopropyl)silane (36.1 g., 2 mole-% based on the amount of silane) were thoroughly mixed and then heated at 70°C. for 72 hr. After cooling to 25°C., the product had a viscosity of 2.4 poise. To this mixture, at 75°C., was added triethylamine (23 g., 1% of the material to be polymerized) and sulfur (186 g., 5.8 mole). The hydrogen sulfide produced by the oxidation was removed under reduced pressure, leaving a polymer with a viscosity of about 12 poise at 25°C.

Preparation of SPS-5

Dimethyl bis(3-mercaptopropyl)silane (20 g.), LP-32 (80 g.), and methyl tris(3-mercaptopropyl)silane (0.5 mole-% based on the amount of silane) were blended in a vessel and heated to 70°C. for 72 hr. Polymerization was not necessary, since the redistributed polymer had the required molecular weight.

CONCLUSIONS

Silane mercaptan monomers, when redistributed with diethylformal polysulfide polymer, produced a glass transition temperature that was 16°C. lower than that of the diethylformal polysulfide polymer alone. In other work performed at the Chemical Division of Thiokol, it was shown that the glass transition temperature of polysulfide polymers is, to a large extent, dependent upon the distance between the polar disulfide groups in the polymer. It, therefore, appears that the silicon atom serves to extend the distance between disulfide groups by virtue of the fact that it is a larger atom than carbon. In addition, the silicon atom, along with its pendant side groups, may also serve as points of discontinuity in the polymer chain to inhibit the formation of crystallites which would degrade the polymer's low temperature physical properties; i.e., increase modulus and decrease strain capacity.

Silicon in the backbone of a polymer chain does cause a sizable increase in the burning rate of the propellant made with the polymer. The quantity of silicon in the polymer is not critical in quantities as low as 2.4%.

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4. E. M. Fettes, U.S. Pat. 2,606,173 (August 5, 1952).

Résumé

Deux monomères mercaptansilaniques ont été polymérisés et préparés par oxydation pour fournir des polymères mercaptés polysulfurés et silaniques. Les monomères mercaptosilanés étaient de formule générale $[\text{HS}(\text{CH}_2)_x]_2\text{SiY}_2$, où $x = 3$ et $\text{Y} = \text{Et}$ ou Me . Ces monomères étaient préparés par addition de thioacétique au diallyldialkylsilanes. Le diacétate thiolé qui en résultait par addition était hydrolysé dans le NaOH alcoolisé pour former le dimercaptan. La polymérisation du dimercaptan était accomplie au moyen de peroxyde, d'iode ou de soufre, fournissant des polymères de poids moléculaires d'environ 1200. Ces polymères étaient transformés en élastomères solides à la suite des agents oxydants doux. Les monomères mercaptans étaient également distribués avec des polymères polysulfures diéthylformaliques qui étaient ensuite transformés en élastomères solides avec des agents oxydants doux. Les polymères redistribués à base de silane-diéthylformal ont été utilisés pour fabriquer des propellants solides composites. Un accroissement de 50% de vitesse de combustion du carburant propulseur et une diminution de 16°C de la température de transition vitreuse a été obtenue lorsque le polymère redistribué était utilisé au lieu du polymère diéthylformalique comme liant du carburant. Les procédés expérimentaux sont indiqués.

Zusammenfassung

Zwei Mercaptosilan-Monomere wurden dargestellt und durch Oxydation zu mercaptan-funktionellen Silanpolysulfidpolymeren polymerisiert. Die Mercaptosilanmonomeren besaßen die allgemeine Formel $[\text{HS}(\text{CH}_2)_x]_2\text{SiY}_2$ mit $x = 3$ und $\text{Y} = \text{Et}$ oder Me . Sie wurden durch Addition von Thioessigsäure an Diallyldialkylsilane dargestellt. Das dabei gebildete Dithiolacetat wurde in alkoholischer NaOH zum Dimercaptan hydrolysiert. Die Polymerisation des Dimercaptans wurde mit Peroxyden, Jod oder Schwefel durchgeführt und lieferte Polymere mit einem Molekulargewicht von etwa 1200. Diese Polymeren wurden mit milden Oxydationsmitteln in feste Elastomere umgewandelt. Die Mercaptan-Monomeren wurden auch mit Diäthylformalpolysulfidpolymeren zur Reaktion gebracht, die dann wieder mit milden Oxydationsmitteln zu festen Polymeren umgesetzt wurden. Die umgewandelten Silan-Diäthylformalpolymeren wurden zur Erzeugung zusammengesetzter Treibstoffe verwendet. Bei Verwendung des umgewandelten Polymeren an Stelle von Diäthylformalpolymeren als Treibstoffbindemittel trat eine 50%ige Erhöhung der Abbrenngeschwindigkeit und eine Erniedrigung der Glasumwandlungstemperatur um 16°C auf. Die experimentellen Verfahren werden beschrieben.

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