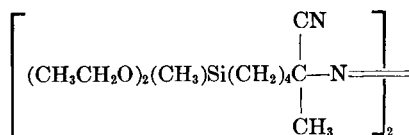


Synthesis of Silicon-Substituted Azonitriles and Their Use in Preparing Caulks

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Synopsis

A silicon-substituted azonitrile,

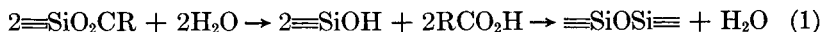


has been synthesized by the hydrosilation of 5-hexene-2-one azine with methylchlorosilane in the presence of chloroplatinic acid, followed by hydrocyanation with anhydrous HCN, and subsequent oxidation with chlorine. The azonitrile is an initiator for radical polymerizations. It is especially useful for the preparation of low molecular weight polymers that, after treatment with acetic anhydride, cure at room temperature in the presence of atmospheric moisture. The preparation of a series of room temperature-vulcanizable materials based on a tetrafluoroethylene/methyl vinyl ether copolymer is described.

INTRODUCTION

In certain respects, the preparation of heat- and solvent-resistant, room temperature-vulcanizable (RTV) caulks is more demanding than the preparation and curing of the corresponding "normal" elastomers. If the material is to be a one-part system, it must cure only when desired, and the crosslinks resulting must be thermally stable at the use temperature. Furthermore, if a high-solids material is desired (for minimal shrinkage), the bulk viscosity of the polymer must be fairly low.

Since high-solids materials are preferable, relatively low molecular weight materials are needed, and it is thus advantageous to place the chain extension and/or crosslink sites at the chain ends. One desirable method that has been used to do this¹ has been the use of a free-radical initiator containing groups that can react to form crosslinks. Furthermore, the relative simplicity of the curing chemistry of silicone caulks, in many cases the hydrolysis of an acyloxysilane,

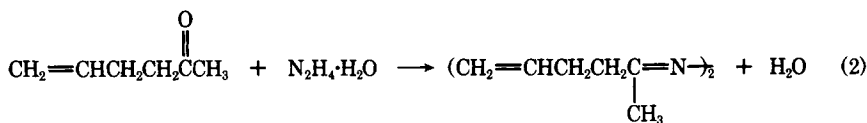


and the good thermal stability of the resulting siloxane crosslink make this type of curing very attractive.

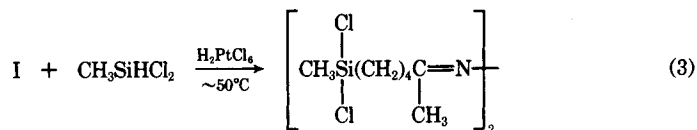
We therefore decided to synthesize an initiator containing moisture-reactive silicon groups which, after appropriate polymerization reactions, would cure by reaction with moisture. Because of the propensity for silicon-oxygen groups to exchange with other oxygen functions (i.e., alcohols, peroxides), it was decided to synthesize an alkoxy-silane-substituted azonitrile in which, during and after the synthesis, there would be little or no exchange between the alkoxy groups and the nitrogen functions of the azonitrile.

SYNTHESIS OF INITIATORS

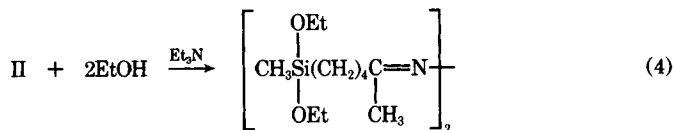
One important consideration in designing the synthesis was that silicon compounds could not be subjected to conditions in which they would hydrolyze. The following synthesis, in which the sequence of reactions is important, was successful:



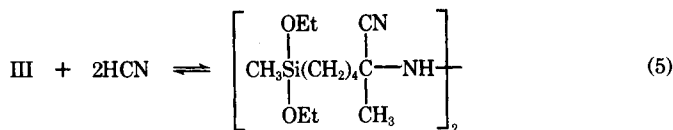
I



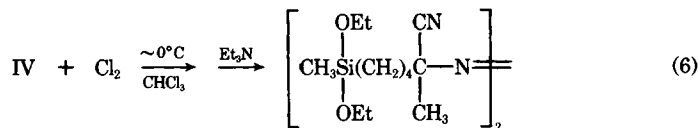
II



III



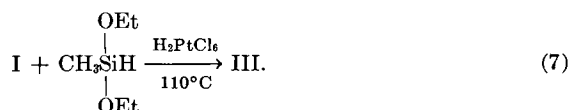
IV



V

5-Hexene-2-one is preferred as the starting material since it is readily available, and unsubstituted terminal double bonds are usually the most

reactive in hydrosilation reactions,² eq. (3). (Other ketones with this structural feature should work, except methyl vinyl ketone.) Reaction (3) is exothermic and may also be performed with dimethylchlorosilane. However, compound II is unstable (the corresponding monochloro compound can be distilled, but it decomposes over a period of several weeks) and cannot be distilled at reduced pressure; II is immediately converted to the distillable dialkoxysilane by reaction with alcohol, eq. (4), in the case depicted, ethanol. The overall yield of steps (3) and (4) is about 70%. Alternatively, dialkoxysilanes may be added to the unsaturated azine directly, eq. (7), although the yields are much more variable (40–70%):



The hydrocyanation is carried out at 75°C with anhydrous HCN, and since the reaction is reversible, the product cannot be distilled. The final step is an oxidation of the hydrazo compound to the azo compound by chlorine in chloroform, the first time to the authors knowledge that this type of oxidation has been carried out in an anhydrous medium. A tertiary amine is then added to remove the by-product HCl as the filterable amine hydrochloride. Each of the last two steps, eqs. (5) and (6), proceed in high yield (>90%).

The silicon-substituted azonitrile appeared to behave as a "normal" azonitrile³ and initiated polymerizations of monomers such as methyl methacrylate, vinyl acetate, styrene, and chloroprene. The half-life of the initiator in nonane at 80.4°C was measured spectrophotometrically by measuring the decrease in the 347-nm band (—N=N—), and was 90 min. By comparison, azobisisobutyronitrile has a half-life of 118 min at 79.8°C in the same solvent.

PREPARATION OF CAULKS

In order to prepare polymers with reactive sites* at both ends derived from a radical initiator, the following reaction scheme must take place (In = initiator fragment, M = monomer):

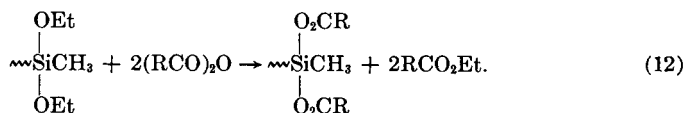


Thus, either step (10) and/or (11) must be the reaction(s) that predominately stops the growth of chains, and not a chain transfer process.

* In order to avoid confusion, reactive sites will refer to the number of silicon atoms, with their reactive groups, per chain, regardless of the number of reactive groups on the silicon atom. The number of reactive groups per silicon atom will be called the functionality.

Furthermore, in order to achieve a narrow molecular weight distribution, the entire polymerization should be carried out in solution.

The first caulk prepared was based on poly(ethyl acrylate). In order to assure that most of the chains contained two reactive sites, a relatively large amount of V (0.012 mole) compared to the amount of monomer (0.51 mole) was used. The material was allowed to cure 34 days at 75% relative humidity and room temperature. At the end of this time, it was cured, although its physical properties were T_B , 56 psi and E_B , 140%, which may indicate that the polymer was either not highly difunctional or completely cured. Also, the cure took undesirably long, so it appeared advantageous to convert the alkoxyisilane groups of the polymer to acyloxyisilane groups by reaction of the polymer with a carboxylic acid anhydride:



Although the preparation of a poly(ethyl acrylate) caulk demonstrated that the system could work, fluorocarbon polymerizations presented some other difficulties. During the preparation of many of the fluorocarbon elastomers so far reported, chain transfer occurs readily, and many polymerizations are not readily initiated by azonitriles, so the choice of polymers is rather restricted. One type of polymer that meets the requirements of the polymerization is that of tetrafluoroethylene (TFE) with alkyl vinyl ethers; and we chose to study the TFE/methyl vinyl ether (MVE) system. Data on various runs are found in Table I.

The most interesting point in Table I is the relationship of molecular weight to the monomer/catalyst ratio. At a high ratio of 1.8×10^3 (run A), it is evident that much chain transfer takes place, owing to the fact that the concentration of radical species is very low. Thus, the bimolecular reactions (10) and (11) do not occur as readily as chain transfer to solvent; such chain transfer is a pseudo first-order reaction due to the high concentration of solvent. However, if the monomer-to-catalyst ratio is decreased to

TABLE I
Preparation of Tetrafluoroethylene/Methyl Vinyl Ether Caulks Using Compound V

Polymer	Moles catalyst $\times 10^2$	Total moles of monomer ^a	\bar{M}_n		% Si	
			Found ^b	Theory ^c	Found ^d	Theory ^e
A	0.044	0.80	47,000	143,000	0.059	0.12
B	1.0	0.80	8,350	6,800	0.99	0.67
C	1.1	0.70	6,800	5,600	1.01	0.83
D	1.1	0.60	5,700	4,800	1.34	1.02
E	1.0	0.50	3,630	4,400	1.62	1.54

^a Equimolar amounts of TFE and MVE were used.

^b By vapor pressure osmometry.

^c Assuming two reactive sites per molecular and no chain transfer.

^d By neutron activation analysis.

^e From experimental \bar{M}_n assuming two active sites per molecule.

50–70 (runs B–E), reactions (10) and (11) become much more favorable in comparison with chain transfer to solvent, since the relative concentration of active radical species during polymerization is increased. The amount of silicon in these materials also indicates that most of the polymer molecules contain two active sites.

The materials listed in Table I were treated with acetic anhydride at 150° for ~16 hr to convert the diethoxysilane to a diacetoxysilane, eq. (12). The resulting caulks (which have consistencies of soft to very firm putties, depending upon molecular weight) were pressed into test pieces. The pieces were placed (in the molds) in a chamber maintained at 75% relative humidity at room temperature. After 2–5 hr, a cured "skin" was evident on the surface exposed to air. The pieces appeared to be fully cured after one week, and typical properties of three gum stocks are given in Table II.

The data indicate that these materials cure well (for caulks) to elastomers that have good physical strength. A few preliminary experiments with fillers indicate that tensile strengths of over 500 psi are easily attainable. The cured caulks appeared to be indefinitely stable at 176°C in air, but seemed to degrade somewhat at 204°C. After two weeks at the latter temperature, decreases in elongation at break were noticeable. "Ordinary" TFE/MVE vulcanizates are stable at 204°C, and the present degradation is probably due to oxidation of the hydrocarbon parts of the initiator fragments, especially $-(CH_2)_4$. The caulks are not appreciably swollen by aliphatic hydrocarbons but are affected by other more polar solvents. The solvent swell pattern is very similar to that for an ordinary TFE/MVE vulcanizate, and thus the endgroups have little effect on the solvent swell properties of the caulk.

Other monomers can be used to prepare low molecular weight polymers that can be cured by moisture. Among these are chloroprene, perfluoro-(methyl vinyl ether)/MVE, TFE/2,2,2-trifluoroethyl vinyl ether, hexafluoropropylene/MVE, etc. The latter three, after curing, have better solvent resistance than TFE/MVE caulks, but have less physical strength, which is probably due to chain transfer which results in less than two reactive sites per chain.

TABLE II
Properties of Cured Caulks

Polymer	B ^a	C	E
Modulus at 100% elongation, psi	55	70	85
Tensile strength, psi	360	350	350
Ultimate elongation, %	420	275	250
Tensile set, %	30	7	10
Shore hardness A	36	27	41
Solvent swell, wt-%			
Octane	-1	0	0
Toluene	102	95	95
Acetone	281	303	303

^a Designations correspond to those in Table I.

EXPERIMENTAL

Preparation of Polymers and Curing

TFE/MVE polymers were prepared in 400-ml bombs, which were charged with 200 ml ethyl acetate and the materials listed in Table I. The bomb was shaken and heated at 85°C for 4 hr. After removing the solution from the bomb, volatiles were removed at 50° and <1 mm Hg pressure in a vacuum oven. Yields were close to 100%. Other vinyl ether polymers were prepared in a similar way.

Some of the polymer (15–20 g) was placed in a resin kettle with a nitrogen atmosphere. Acetic anhydride (5–10 ml) was added, and the contents were stirred and heated to ~150°C. After ~16 hr at 150°, the volatiles were removed under vacuum, and a test piece was prepared. The caulk was allowed to cure seven days at 75% relative humidity and 25°, although a cured "skin" had usually formed after 2–5 hr. Physical properties of the cured polymers are given in Table II.

Ethyl acrylate (55.0 ml) was polymerized by adding a solution in benzene (~100 ml) to a refluxing benzene (400 ml) solution of 6.0 g of compound V over a period of 2 hr and then refluxing another hour. The solvent was removed under vacuum on a rotary evaporator, leaving a mobile liquid which was poured into a mold. A polychloroprene polymer was prepared in a similar manner.

5-Hexene-2-one Azine (I)

To a 500-ml round-bottom flask was added 98 g 5-hexene-2-one and 25 g hydrazine hydrate (the reaction is exothermic). The mixture was stirred and refluxed for 6 hr. At the end of that time, the organic layer was separated, dried over anhydrous MgSO₄, filtered, and distilled on a spinning band column. The yield was 74.1 g (77%). The properties and analyses of I and the other new compounds are given in Table III.

6-(Methyldiethoxysilyl)hexane-2-one Azine (III)

To a 500-ml three-necked round-bottom flask equipped with a condenser, magnetic stirrer, 250-ml addition funnel, and thermometer, and containing a nitrogen atmosphere, were added 144 g 5-hexene-2-one azine and 2 drops of saturated aqueous chloroplatinic acid. Methyldichlorosilane (172 ml) was poured into the addition funnel, and 15 ml of that was added to the flask. An exothermic reaction took place, and during the addition (1.25 hr) the temperature was controlled to 50–60°C by use of a wet ice bath. After stirring for an additional 1.5 hr, the crude reaction mixture was transferred to a 3-liter three-necked round-bottom flask equipped with condenser, mechanical stirrer, and 250-ml addition funnel. Under nitrogen, the flask contents were diluted with 1 liter hexane and 456 ml triethylamine. Ethanol (192 ml) was then added dropwise to the flask over a period of 1.5 hr. The reaction was exothermic as evidenced by refluxing of solvent, and the mixture became quite viscous and difficult to stir because of the solid which formed.

TABLE III
Properties and Analyses of New Compounds

Com- pound	bp/pressure °C/mm Hg	n _D temp., °C	C, %		H, %		N, %		NMR spectra ^a
			Theory	Found	Theory	Found	Theory	Found	
I	130/23	1.4786 (26)	75.0	74.9	10.5	10.4	14.6	14.4	0.27 (s, 6); 0.7 (m, 4); 1.18 (t, 12); 1.35- 2.57 (m, 20); 3.71 (q, 8).
III	148-158/0.2	1.4517 (25)	57.2	56.5	10.5	10.1	6.1	6.7	
IV			56.0	55.4	9.8	9.6	10.9	10.7	
V ^b			56.2	54.3	9.4	8.9	10.9	11.0	0.09 (s, 7); 0.52 (m, 4); 1.0-2.0 (m, 28); 3.67 (q, 8) 0.11 (s, 6); 0.55 (m, 4); 1.3-1.7 (m, 33); 3.65 (q, 8)

^a In benzene. First value is position (in δ) from TMS (type s = singlet, t = triplet, q = quartet, m = multiplet, then number of protons).

^b Ultraviolet spectrum, $\lambda_{\max} = 347 \text{ m}\mu$, $\epsilon = 21$ (chloroform).

After stirring overnight, the mixture was filtered, the filtrate washed twice with water, dried over anhydrous K_2CO_3 , filtered, and the solvent removed under vacuum on a rotary evaporator. Upon distillation, 233 g 6-(methyldiethoxysilyl)hexane-2-one azine (III) was isolated.

Compound III may also be prepared directly by the chloroplatinic acid-catalyzed hydrosilation of I by methyldiethoxysilane at 100–110°. This reaction is exothermic, and the temperature is maintained by addition of the methyldiethoxysilane.

1,2-Bis(6-methyldiethoxysilyl-2-cyano-2-hexyl)hydrazine (IV)

Into a 400-ml bomb were loaded 65 g 5-methyldiethoxysilylhexan-2-one azine and 60 ml HCN. The bomb was sealed and heated at 75° for 4 hr. The bomb was emptied, and the material, now an orange liquid, was transferred to a 300-ml flask. The HCN was removed by applying a vacuum (0.5–1.0 mm) for 2 hr while the flask was immersed in a wet ice bath. At the end of this time, the liquid was much more viscous.

Azobis-2-(6-methyldiethoxysilyl-2-cyano-2-hexyl)hydrazine (V)

Into a 1-liter, three-necked round-bottom flask equipped with condenser, magnetic stirrer, gas inlet tube, and thermometer, and under nitrogen, were added 114 g 1,2-bis(6-methyldiethoxysilyl-2-cyano-2-hexyl)hydrazine and ~600 ml chloroform that was freshly chromatographed over silica gel. The flask was cooled to ~-8° in a NaCl-wet ice bath, and then chlorine was bubbled in during four separate periods of 3–5 min each. The temperature during this time was -8° to -2°. After each chlorine addition, a drop of solution was removed and tested with wet (water) starch-iodide paper. At the end of the fourth addition, the characteristic blue color indicative of free chlorine was noted.

The flask contents were then subjected to a vacuum for 45 min (removing most of the chloroform), and then 35 ml pyridine was added; the orange solution was stirred for 1 hr and then added to 2 l. of pentane. A white precipitate formed, and the yellow solution was placed in a freezer overnight.

The next day, the mixture was filtered and the solvent was then removed under vacuum from the filtrate on a rotary evaporator overnight. The yield of yellow liquid was 105 g (95%).

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