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ANNUAL REPORT

HIGH ENERGY ELASTOMERIC POLYMERS

(1 May 1977 through 30 April 1978)

Research sponsor:
Office of Naval Research
Power Branch
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Contract N00014-75-C-0791
Project NR 093-054

Prepared by

Robert S. Neale

24 May 1978

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The overall goal of the work described is to increase the energy content of potential binder polymers useful in the compounding of solid propellant or explosive compositions. The underlying technical principle is that the high energy (HE) modification of pre-formed, linear backbone structures is believed to offer more potential for achieving elastomeric polymers than the direct polymerization of HE monomers. Substantial progress has been made this year in the preparation of aminoalkylsilicone

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20. Abstract (cont'd)

receptor polymers and their one-step reactions with fluorodinitroethanol (FDNE) to afford HE derivatives, whose further conversion to elastomeric products is now under active study. The polysiloxane skeletal framework was selected first for energization because of its often superior flexibility and stability within a wide temperature range.

The HE derivatization of the receptor polymers is being accomplished via one-step, Mannich condensations of FDNE with primary or secondary amino groups in the side chain alkyl residues. The synthesis and analysis of such aminoalkylsilicones bearing various side chains R, e.g., $-\!\!(\mathrm{Si(Me)(R)O})\!\!-_{x}$, has progressed well; representative silicones have been prepared with R-groups equal to 4-aminobutyl, 3-aminopropyl, aminomethyl, and 3-ethylenediaminopropyl. Good progress has also been made in maximizing the number of linear vs. cyclic units in these receptor polymers.

FDNE has been readily introduced into some of the aminoalkylsilicones to yield viscous HE polymers with 1 or 2 FDNE residues per spinal Si atom. Thus, in the aminobutyl system, molecular weights have reached approximately 10,000, and HE derivatives have been prepared using both nitrogen centers in the ethylenediaminopropyl system to increase the energy loading per siloxane spinal unit. Several monomeric aminoalkylsilane esters have also been condensed with FDNE, and some initial oligomer gelation studies in the HE aminobutyl system have been promising.

Methods suitable to the analysis of the polymer product mixtures have been developed. Differentiation between cyclic (3,4, and 5 silicons per ring), internal linear, and terminal linear (SiOH) species has now been achieved by 29-Si-nmr spectroscopy, and progress has been made in the determination of molecular weights of these unusual materials. Product densities have been observed in the range of 1.3 - 1.4 g/cc (kg/m^3). Some differences in thermal stability have been noted and are under study in the amino vs. ethylenediamino systems.

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SUMMARY

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INTRODUCTION AND BACKGROUND

In Part II of our previous Annual Report,(1) we first presented the concept and described some supporting experimental work for the synthesis of organosilicone and other backbone polymers containing high-energy (HE) side-chain residues. We now report further work on this subject performed during the period May, 1977, through April, 1978. The discussion contained herein will be documented by experimental details in a technical report or paper for publication to be written later; a summary precedes each of the following major sections of results.

The rationale behind this work was as follows. Several high-energy monomers based on 2, 2, 2-fluorodinitroethanol (FDNE) had been made in recent years, including the silane esters prepared by the author under the present ONR contract.(1) These compounds have been of interest as HE plasticizing and stabilizing additives in explosive or controlled-burn compositions containing particulate HE solids. When such plastic materials are to be used as fuels, however, a binder polymer is also required. This must be of a nature to impart bulk strength and creep resistance to the propellant charges during handling and storage. Further, through a controlled balance of cross-linking vs. linear molecular weight, a rubbery, elastomeric nature must be retained over a substantial temperature range in order to provide adequate resistance to mechanical shock.

Ordinary elastomeric binders have been comprised largely of hydrocarbon, acrylate, or urethane polymers, which contain insufficient oxidizing power for auto-combustion and hence detract from the energy output that would otherwise be developed in compositions containing them. Binders having increased energy content have therefore been envisioned wherein polymers contain a sufficient number of oxidant groups to provide a substantial part, or possibly all, of the energy needed for their combustion to gaseous products.

Examples of several types of such energy-enriched polymers have been published in recent years. In most cases, these materials have actually constituted prepolymers for use in subsequent curing reactions in the presence of solid explosives, and any post-cure elastomeric properties have not been revealed. When high polymers have been obtained and their properties reported, the results have not been encouraging, since the T_g have been well above room temperature and the energy contents and and tensile strengths relatively low. In most instances, the approach followed has been to prepare monomeric HE compounds for subsequent free radical or condensation polymerization to hydrocarbon polymers, e.g., polyacrylates (2-8) and polyvinyl ethers (9), or to polyethers (10) or polyesters (11). High molecular weights have proved elusive in these studies, however, since the facile polymerization of such monomers is severely inhibited by the presence of bulky and electronically complex functional groups.

To overcome this apparent bar to the preparation of HE binder polymers, we proposed a new approach, and work carried out during the past year has confirmed its potential. Thus, we have pursued the concept of first preparing high molecular weight or chain-extendable spinal chains bearing functional side groups and only then introducing pre-formed HE moieties in a single step reaction.

OVERVIEW OF RESULTS

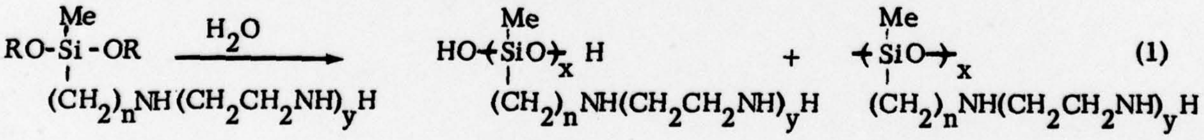
Work during the past year has focussed on polysiloxane backbone structures for their potentially favorable temperature vs. flexibility and stability properties. Other systems which fall under our general concept of polymer preparation followed by introduction of intact oxidant groups have not yet been examined. As proposed, we have adopted the efficient Mannich condensation of 2,2,2-fluorodinitroethanol (FDNE) with side-chain aliphatic amino groups as the key reaction for the one-step introduction of HE residues into silicone polymers. The bulk of our work has been limited by time to the first two of the following four necessary areas of investigation, although the third area has received preliminary attention.

- Preparation and analysis of precursor silicone polymers;
- Introduction of FDNE groups and analysis of the resulting polymers;
- Chain extension or crosslinking to higher molecular weight, elastomeric products;
- Determination of some physical properties of elastomeric products.

Our first objective was to prepare a number of silicone polymers bearing differing types of aminoalkyl side chains as receptor precursors to the ultimate HE derivatives. A second objective was to demonstrate the feasibility of preparing the desired FDNE-based derivative polymers. A concurrent, third objective was to develop methods for analyzing the natures of the polymeric structures generated. We have largely succeeded in meeting these objectives.

PRECURSOR SYNTHESIS: AMINOALKYLSILICONE POLYMERS

Section Summary - Precursor silicone polymers, II, have been synthesized according to eq. 1 as receptors for the attachment of FDNE groups at the nitrogen atoms of the pendant aminoalkyl side chains. The silicones II were prepared by hydrolysis of the bis-ethoxy or methoxy silane esters I, which were obtained by various methods. Only the starting silane ester I-C has posed a difficult problem, as discussed below.



$$\underset{(CH_2)_nNH(CH_2CH_2NH)_yH}{RO\text{-}\overset{Me}{Si}\text{-}OR} \xrightarrow{H_2O} HO\text{-}(\underset{(CH_2)_nNH(CH_2CH_2NH)_yH}{\overset{Me}{Si}O})_x\text{-}H + (\underset{(CH_2)_nNH(CH_2CH_2NH)_yH}{\overset{Me}{Si}O})_x \quad (1)$$

I　　　　linear II　　　　cyclic II

Example	n	y	Type
A	4	0	Aminobutyl
B	3	0	Aminopropyl
C	1	0	Aminomethyl
D	3	1	(Ethylenediamino) propyl
E	1	1	(Ethylenediamino) methyl

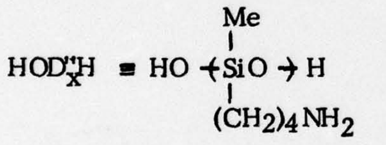
We have now obtained and studied to varying degrees examples of types A-D of general structures I and II; the type E system will be addressed shortly. Both linear and cyclic forms of II were generated during hydrolysis. The chain length, x, of the linear form varied with the nature of the side chain and the conditions of hydrolysis or catalyzed post-equilibration of the initial products.

The bulk of the groundbreaking work was carried out in the relatively accessible aminobutyl system A, with which we had already had some experience. More recently, we have prepared examples of the aminopropyl and aminomethyl systems B and C, in which the number of energy-diluting CH_2 groups, n, has been reduced. Interest in polyaminoalkyl side chains present in type D and E silicones derives from the potential for attachment of FDNE residues at each N atom, thereby increasing the built-in oxidant concentration per spinal -SiO- unit.

Molecular weights of $\sim$ 5000 have been achieved in the linear portions of II-A, as additional polymerization studies continue. The precursor silicones II-B, C, and D have all been obtained under hydrolysis conditions which have afforded largely cyclic products. The generation of largely linear structures analogous to what we have now achieved in the model case, II-A, is under study.

Aminobutyl Side Chains (Type A)

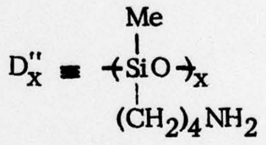
Cyclic and hydroxyl-terminated linear silicones of the type II-A were prepared by hydrolysis of delta-aminobutyl(diethoxy)methylsilane, I-A, as described below (eq. 2). In the discussion of these and other results, we shall occasionally be using the following shorthand notation for repeating polymer units, such as shown for II-A. The symbol D'' will refer to one unit in a $\left(\overset{|}{\underset{|}{Si}}O \right)_x$ chain wherein the difunctional silicon bears one methyl and one aminoalkyl group.



$$HOD''_xH \equiv HO \left(\overset{Me}{\underset{(CH_2)_4NH_2}{Si}} O \right) H$$

linear II-A

and



$$D''_x \equiv \left(\overset{Me}{\underset{(CH_2)_4NH_2}{Si}} O \right)_x$$

cyclic II-A

Prior to presenting the hydrolysis results, we should note two relevant, general aspects of polysiloxane formation. First, in silane ester hydrolyses, one can normally prepare only a mixture containing both cyclic and linear polysiloxanes. The tendency toward cyclization increases with increasing side chain bulk and dilution of spinal SiO units in a solvent or in the polymer itself, and one cannot efficiently polymerize bulky cyclics, once formed, to long chain linears by catalytic ring-opening reactions.(12) In fact, cyclic diorganosilicones bearing even very small groups, including dimethylsilicones, still contain cyclics when fully equilibrated, although ring-opening may be faster than the reverse process and afford some measure of kinetic control over the mixture composition. Usually, cyclics also persist in the presence of added endblocker species. If one can strip volatile cyclics from a crude hydrolysate, the residual HO-ended linear units of the mixture can then be chain-extended by reaction with condensing agents. More generally, but less simply, linear oligomers can first be prepared by specific syntheses and then suffer polymerization through various end group chemistries. When cyclics cannot be stripped out, as in the present work with the high-boiling aminoalkylsilicones, their concentration can often be minimized to the point where their unavoidable presence is not detrimental to the final polymer properties sought.

A second characteristic of the systems under study is that the aminoalkylsilicones contain built-in amino group catalysts for effecting base-catalyzed silanol condensations or, under much more rigorous conditions, siloxane bond equilibrations in some cases. This can be an advantage at times, but a disadvantage when catalyst poisoning or removal is desired. Very little work has been done in the past on the preparation of homogeneous aminoalkyl (methyl) silicone polymers; normally, such materials are diluted by co-formation with dimethylsilicone or similar units. It has therefore been necessary for us to define methods of preparing aminobutyl (methyl) silicones of high linearity as both precursors for functionalization with FDNE and as models for less readily accessible, homologous silicones containing fewer methylene groups in the side chain.

Two approaches to highly linear aminobutylsilicone mixtures have been pursued experimentally: the hydrolysis of I-A directly (eq. 2), and the catalyzed post-equilibration of the cyclic and linear hydrolysates II-A to at least moderately high molecular weight oligomers suitable for chain extension through the end groups. It should be noted that all the product mixtures produced consisted of a mixture of polymeric species, whose analysis is discussed in a separate section.

$$\underset{\text{I-A}}{(EtO)_2MeSi(CH_2)_4NH_2} \xrightarrow{H_2O} \underset{\text{(cyclic + linear) II-A}}{D''_x + HOD''_xH} + EtOH \qquad (2)$$

The hydrolysis of I-A has been conducted under varied conditions which were found to favor cyclics formation in one case but linears in another. In the former preparation, silane I-A was boiled with 4 moles of water in the presence of Me_4NOH, a siloxane bond rearrangement catalyst, and the liberated ethanol was distilled out at a pot temperature not exceeding 95°C. To remove water and the remaining ethanol, toluene was added to the cooled mixture and then slowly distilled at a pot temperature of 150° to maximally dehydrate the system and decompose the catalyst. Further work-up yielded a product rich in cyclics rather than the high molecular weight, linear silanol condensation products desired. The material contained approximately 80% of a mixture of D''_4 and and D''_5 along with approximately 20% of linear species of average molecular formula approximately HOD''_7H. If one distills the cyclics, a mixture $D''_{3,4}$ is obtained, wherein the D''_3 component (only) undergoes a spontaneous ring opening reaction upon contact with water.

Another hydrolysis of I-A was conducted, this time in the absence of the strongly basic catalyst and azeotropic distillation with toluene. The amino groups of the silane are sufficiently basic to catalyze the hydrolysis and silanol condensation reactions, but should not afford ring-opening or chain equilibration under mild conditions. Simple stripping of the boiled reaction mixture gave a product now found to contain only ~ 25%

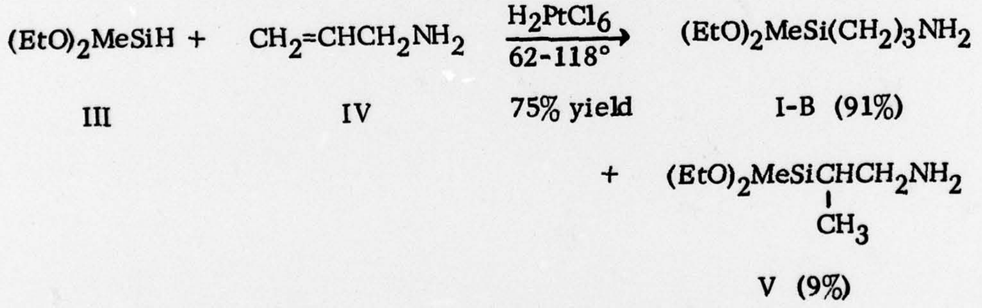
of cyclic and ~ 75% of linear type silicon atoms. Analysis suggested an average linear molecule to be $HOD''_{34}H$ (number average molecular weight $M_{\bar{N}}$ ~ 4450) or $HOD''_{62}H$ ($M_{\bar{N}}$ ~ 8100), depending on spectral interpretation (see p. 13). Both hydrolysates were used in the preparation of HE derivatives, as described in the appropriate major section below.

Experiments have also been carried out whose goal was to achieve the maximum linear polymerization of these aminobutyl hydrolysates. Treatment of the high cyclics hydrolysate with 5 moles of water and 1 mol % KOH catalyst at 90° gave a clear solution which was then cooled, neutralized with 2 eq of 1 $\underline{N}$ H_2SO_4 per eq KOH, and stripped under vacuum at 45° after the addition of 0.3 volume of toluene. The product was now similar to the high linears material obtained directly from the hydrolysis of I-A, except for a 2 to 3-fold higher silanol group content.

Small samples of all three of the aminobutylsilicone products just described were subjected to varying catalysts and reaction conditions in further pursuit of increasing the wt % and $M_{\bar{N}}$ of the linear portion HOD''_xH. The results, currently under analysis, will serve as a guide to the potentially most favorable treatment for polymerization of other aminoalkylsilicone hydrolysates. It appears at the moment that the realized molecular weight increases were generally less than 5-fold, i.e., relatively small. Chain extension by chemical reaction may thus be the only means in these systems to achieve the high $M_{\bar{N}}$ values supposedly necessary for the generation of elastomers possessing reasonable tensile strength.

Aminopropyl Side Chains (Type B)

The silane ester, I-B, required for hydrolysis to siloxanes II-B, was prepared by Pt-catalyzed addition of diethoxymethylsilane, III, to allylamine, IV (eq. 3). About 9% of the β-isomer V accompanied the main product, I-B, regardless of the reaction conditions. Hydrolysis of a sample



$$\begin{array}{ccccc} (EtO)_2MeSiH\ + & CH_2{=}CHCH_2NH_2 & \xrightarrow[62\text{-}118^\circ]{H_2PtCl_6} & (EtO)_2MeSi(CH_2)_3NH_2 & \\ \text{III} & \text{IV} & \text{75\% yield} & \text{I-B (91\%)} & \\ & & + & (EtO)_2MeSi\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2NH_2 & (3) \\ & & & \text{V (9\%)} & \end{array}$$

of an 86:14 mixture of I-B and V at room temperature with no added catalyst quantitatively afforded a largely cyclic product $D''_{4,5}$. We expect this to be convertible to a high linears material in a manner analogous to that being worked out for the aminobutyl cyclics.

Aminomethyl Side Chain (Type C)

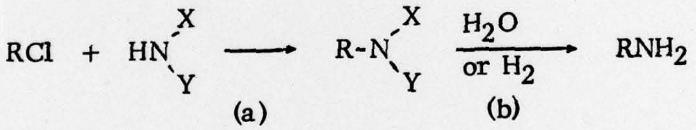
In contrast to its higher methylene homologs, the silane ester monomer I-C has resisted both facile synthesis and straightfoward hydrolysis. Considerable time has been spent in dealing with the aminomethyl system, however, since the HE derivatives of polysiloxanes bearing $-CH_2NH_2$ side chains should be the least diluted by energy-absorbing hydrocarbon residues.

Monomer synthesis - The problem was to utilize the chloride $(EtO)_2MeSiCH_2Cl$, VI, as the starting material. Thus, hydrosilylation of an olefinic amine (propyl system) or cyanide (butyl system, i.e., allyl cyanide followed by reduction) is obviously inapplicable to the monomethylene system, and the chloromethyl compound VI is by far the most readily accessible starting material. We have studied both the direct conversion of VI to I-C by ammonia and indirect procedures involving a blocked ammonia compound, followed by deblocking.

Unfortunately, we have confirmed that the direct amination is indeed as inefficient as reported, (13) but we have used it nevertheless to obtain material with which to initiate the hydrolysis studies. Thus, reaction of VI and a 20-30-fold excess of NH_3 in a rocking autoclave at either 60° or 100° led to 100% conversion of VI and a 90 wt % yield of a crude product mixture, but only 40% of the desired I-C could be isolated by distillation. Also formed was 15-40% of the dialkylation product VII (eq. 4). We suspect that use of a solvent to render the silane chloride and liquid ammonia more mutually soluble might reduce the polyalkylation, but it could never do so sufficiently cleanly to permit the use of the reaction on any but a mono-chloroalkyl compound. The conceptually attractive direct amination of poly (chloromethyl) siloxanes generated from the hydrolysis of VI would therefore fail due to the generation of cross-linked gels resulting from polyalkylation side reactions.

$$\underset{\text{VI}}{(EtO)_2MeSiCH_2Cl} + NH_3 \rightarrow \underset{\text{I-C}}{(EtO)_2MeSiCH_2NH_2} + \underset{\text{VII}}{[(EtO)_2MeSiCH_2]_2NH} \qquad (4)$$

The indirect synthesis of primary amines takes the form of eq. 5, in which an amine derivative is cleanly mono-alkylated in a first step. Polyalkylation is



$$RCl + HN\begin{matrix}X\\Y\end{matrix} \xrightarrow[\text{(a)}]{} R\text{-}N\begin{matrix}X\\Y\end{matrix} \xrightarrow[\text{or } H_2]{H_2O} RNH_2 \qquad (5)$$

(b)

prevented by the blocking groups X and Y, which can include a variety of structures amenable to hydrolytic or reductive cleavage in the second, unblocking step. Various amide, imide, isocyanate, and azide compounds have been employed, but none appeared to meet our requirements for large-scale use. Thus, from our early experience (1) with the traditional Gabriel synthesis, which uses phthalimide, (14) we set four requirements in using reaction 5 to prepare aminomethylsilicon compounds from chloromethyl precursors. Step 1 of the procedure must involve largely soluble reactants, be applicable to chlorides as well as the normally used, more reactive bromides, and utilize a blocked amine readily prepared in large quantity. Further, Step 2 should proceed under mild conditions, preferably homogeneously, in order to preserve the structural organization of the organosilicon R residue and be applicable to poly (chloromethyl) silicon compounds as well as monomers. This was a tall order, which we pursued using the potassium salt of trifluoroacetamide as the aminating agent (eq. 6).

$$RCl + \underset{\text{VIII}}{KNHCOCF_3} \xrightarrow[\text{(a)}]{} \underset{\text{IX}}{RNHCOCF_3} \xrightarrow[\text{(b)}]{H_2O} RNH_2 + CF_3COOH \qquad (6)$$

We hoped to achieve monoalkylation exclusively at nitrogen by using the preformed amide salt VIII and take advantage of the known,(15) facile hydrolysis of the product trifluoroacetamides, IX, by dilute base at room temperature. After much study of Step 1 with Me_3SiCH_2Cl as a simplifying model for establishing whether reaction 6 had the potential for general use, we concluded that it probably did not. Thus, reaction 7 was very cleanly achieved in anhydrous dimethoxyethane solvent with equimolar reactants as shown, but side reactions, including probable dialkylation to give XI and nonproductive loss of VIII to the free amide and a nitrogen-free salt, could not be overcome. Further, the limited conversion of the chloride could not be countered effectively by an excess of the salt VIII, and VIII could not be made in pure form. Confirmation of the structure of XI and identification of the nitrogen-free salt as potassium trifluoroacetate remain pending. None of the desired amide product analogous to X was obtained from a reaction between VIII and $(EtO)_2MeSiCH_2Cl$ (VI), which reacted even less completely than the trimethyl model.

$$\underset{80\%\ \text{conversion}}{Me_3SiCH_2Cl} + \underset{\text{VIII}}{KNHCOCF_3} \xrightarrow[85°,\ 4\ \text{hr}]{\text{DME}} \underset{\text{X},\ 66\%}{Me_3SiCH_2NHCOCF_3} + \underset{78\%}{KCl}$$

$$+ \underset{\text{XI},\ \sim 12\%}{[Me_3SiCH_2]_2NCOCF_3} \qquad (7)$$

Hydrolysis - The hydrolysis of $(EtO)_2MeSiCH_2NH_2$ has proved, like the monomer synthesis, somewhat less than straightfoward. An initial attempt under mild conditions (water, ethanol, 0-25°) led to nearly complete ester hydrolysis but also to ~40% of CH_2NH_2 group cleavage from silicon. Later hydrolyses overcame the cleavage but produced an unexpectedly solid product with a melting range of only a few °C and very unusual solubility characteristics; characterization of this material, presumably D''_3, D''_4, or HOD''_3H, is currently in progress. An aminomethylpolysiloxane substrate should thus soon be available for treatment with FDNE.

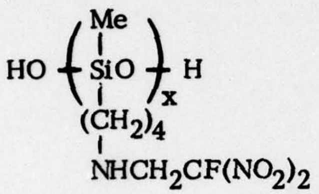
(Ethylenediamino)propyl Side Chains (Type D)

Receptor silicones of structure II-D offer the potential for attachment of a HE group at each of the two nitrogen atoms in the side chain, thereby enhancing the energy loading per silicon atom and decreasing the average number of methylene groups per HE group relative to the aminobutyl type A materials. The hydrolysis precursor, XII, is available commercially and has been prepared readily in the laboratory. The hydrolysis of XII under mild conditions (eq. 8) gave a product containing a high proportion of cyclics $D''_{4,5}$ (> 50%) and apparently some low molecular weight HO-terminated linear species. This material will be subjected to the ring opening conditions found most effective in the aminobutyl case. Meanwhile, mono- and difunctionalization of the present hydrolysate has been carried out with FDNE, as described in the following major section.

$$\underset{\text{XII}}{(MeO)_2MeSi(CH_2)_3NH(CH_2)_2NH_2} \xrightarrow{H_2O} \underset{(\text{cyclic} + \text{linear})\ \text{II-D}}{D''_{4,5} + HOD''_xH} + MeOH \qquad (8)$$

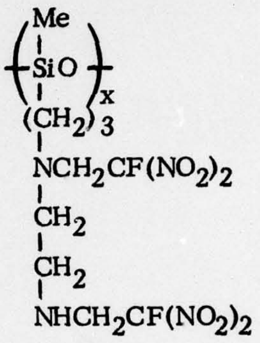
PREPARATION OF HIGH ENERGY POLYSILOXANES

Section Summary - Two of the aminoalkylsilicones have been derivatized by reaction with stoichiometric amounts of FDNE at room temperature; work on the others is in progress. In the aminobutyl series, both the highly cyclic and highly linear forms of silicone II-A were converted to the corresponding HE materials; little or no change in the backbone siloxane structures occurred. The mainly linear HE product XIII-a contained HO- end groups and ~ 34 repeating units per average chain; the $M_{\bar{N}}$ (linear portion) was ~ 9100. The ethylenediaminopropyl silicone II-D also reacted cleanly, this time with 2 moles of FDNE, to generate XIV. These results confirm the relative simplicity and attractiveness of our general approach to HE polymers by 1-step modification of appropriately reactive polymers with energy-rich groups. Further, the density of ~ 1.3 and 1.4 g/cc observed in XIII and XIV, respectively, was substantially higher than that (0.97 g/cc) of ordinary high molecular weight dimethylsilicones, which is important to the effective utilization of the energy content.



$$HO\left(\begin{array}{c}Me\\|\\SiO\\|\\(CH_2)_4\\|\\NHCH_2CF(NO_2)_2\end{array}\right)_x H$$

XIII-a

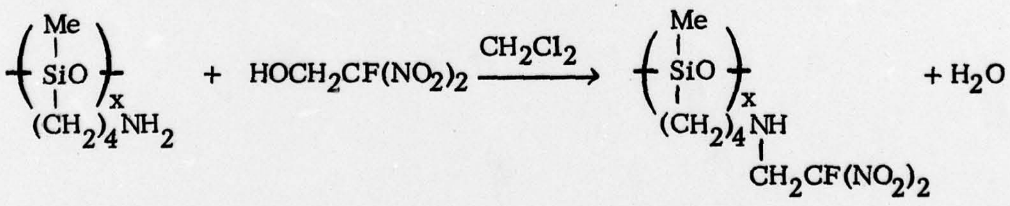


$$\left(\begin{array}{c}Me\\|\\SiO\\|\\(CH_2)_3\\|\\NCH_2CF(NO_2)_2\\|\\CH_2\\|\\CH_2\\|\\NHCH_2CF(NO_2)_2\end{array}\right)_x$$

XIV

HE Aminobutylsilicones

Both the highly cyclic and highly linear samples of the aminobutylsilicone hydrolysate II-A reacted readily and essentially quantitatively with the stoichiometric amount of FDNE in methylene chloride at room temperature (eq. 9). The liberated water was removed with a drying agent prior to vacuum stripping to leave the residue products XIII, which contained both cyclic and linear (XIII-a) species.



$$\left(\begin{array}{c}Me\\|\\SiO\\|\\(CH_2)_4NH_2\end{array}\right)_x + HOCH_2CF(NO_2)_2 \xrightarrow{CH_2Cl_2} \left(\begin{array}{c}Me\\|\\SiO\\|\\(CH_2)_4NH\\|\\CH_2CF(NO_2)_2\end{array}\right)_x + H_2O \quad (9)$$

II-A FDNE XIII

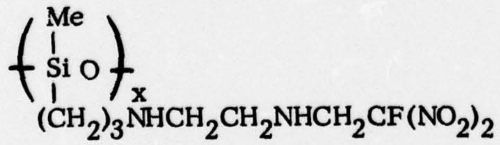
No unreacted FDNE could be detected spectrally, but the formal impurity, $CH_3OCH_2OCH_2CF(NO_2)_2$, present in the starting FDNE, was readily observed in XIII.

Other analyses showed that no substantial change in the relative types of polysiloxane structural units had occurred, although the $M_{\bar{N}}$ observed were about 2 times greater than calculated simply for the addition of the FDNE residues; a larger increase vs. theoretical occurred during derivatization of the high cyclics than with the high linears precursor. Overall, $M_{\bar{N}}$ values ~5850 (high linears) and 2670 (high cyclics) were observed, and the $M_{\bar{N}}$ calculated for just the linear portion of the largely linear product was ~ 9100 [or ~ 16,500, depending upon the (presently uncertain) spectral identification of one component as a cyclic D_6'' or linear species]. Preliminary efforts to chain extend and/or crosslink these materials are described in a later major section. Both products have proved completely stable, at least at room temperature, and are yellow, viscous fluids of density (23°C) ~ 1.30 g/cc.

HE (Ethylenediamino)propylsilicones

The largely cyclic hydrolysate II-D was treated with 1 vs. 2 moles of FDNE in methylene chloride at room temperature, with somewhat diverse results. The 2:1 reaction proceeded normally and quantitatively to afford a thick, lemon yellow grease, XIV, d 1.40 g/cc. Proton nmr analysis was straightforward and strongly in support of the structure XIV, but Si-nmr data proved touchy to acquire. The product appeared to consist largely of cyclics, but possibly of varied configurations. A disposition toward very slow decomposition was observed in this product after some days at room temperature, when sampling led to the slow formation of microbubbles on the glass pipette walls.

When treated with only 1 mole of FDNE, silicone II-D yielded only 95% of the theoretical weight of XV. An unusual, sticky substance, later found soluble in methanol, clung to the Na_2SO_4 drying agent despite repeated rinsings with methylene chloride. The residue product was now red, rather than the usual yellow, and after 3 days at room temperature had developed a tough skin, a modest amount of bubbles, and a greatly increased viscosity to the borderline of immobility. When probed with a glass rod, a cascade of localized microbubbles formed in a few minutes, to an extent significantly greater than observed in the 2:1 product. The material required 8 hours for complete re-solution in methylene chloride.

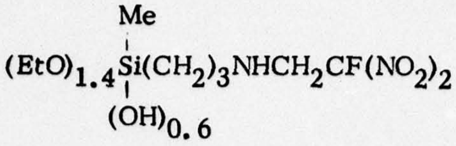


$$\left(\begin{array}{c} \text{Me} \\ | \\ \text{Si O} \\ | \end{array} \right)_x \quad (CH_2)_3NHCH_2CH_2NHCH_2CF(NO_2)_2$$

XV

Reactions of Aminopropylsilane Esters with FDNE

It was of interest to determine whether the water liberated in Mannich reactions such as eq. 9 could effect the efficient in situ hydrolysis of aminoalkylsilane ester monomers and what would be the natures of the resulting products. Only small cyclics would be expected . Reaction of diethoxyaminopropylsilane I-B with FDNE in methylene chloride yielded the average structure XVI, whose spectral analysis suggested the loss of only 30% of the ethoxy groups. The dimethoxy(ethylenediamino)propylsilane I-D, however,

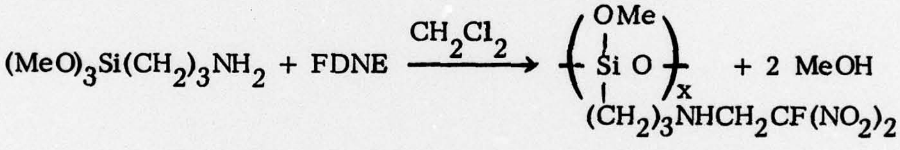


$$\begin{array}{c} Me \\ | \\ (EtO)_{1.4}Si(CH_2)_3NHCH_2CF(NO_2)_2 \\ | \\ (OH)_{0.6} \end{array}$$

XVI

reacted under similar conditions with 2 moles of FDNE to give an essentially fully hydrolyzed product with ~90% alkylation by FDNE. Presumably similar to XIV, this product was not analyzed for siloxane structure by 29-Si-nmr because of the pronounced effervescence of the sample. Again accelerated by contact with a glass rod or stainless steel spatula, the slow gas evolution continued in the neat, orange sample at room temperature; no characteristic odor of the gas could be recognized. The insolubility of XVI in $CDCl_3$ was overcome with a few drops of d_6-DMSO prior to recording the H-nmr spectrum. The sample readily redissolved in methylene chloride.

As expected, the trimethoxy(aminopropyl) silane XVII reacted readily with FDNE as had the I-B and I-D compounds just noted, but the theoretical hydrolysis of just 2 of the 3 MeO- groups (eq. 10) was not cleanly approached. Thus, on average, the fluid product XVIII contained one MeO- group per silicon, but further analysis showed XVIII to consist of a mixture containing 3, 2, 1 and 0 MeO- groups bound to Si. This product may prove to be a useful gelation agent for other HE silicone polymers, however, or exhibit useful properties of its own upon further study.



$$(MeO)_3Si(CH_2)_3NH_2 + FDNE \xrightarrow{CH_2Cl_2} \left(\begin{array}{c} OMe \\ | \\ Si\,O \\ | \\ (CH_2)_3NHCH_2CF(NO_2)_2 \end{array} \right)_x + 2\,MeOH \qquad (10)$$

XVII

XVIII (d 1.40 g/cc)

Miscellaneous Reactions

An alternative route to the compound XVI, but with both ethoxy groups intact, would be the hydrosilylation reaction 11. The HE allylic amine XIX was prepared (16) from allylamine and FDNE in ~ 90% yield (distilled); XIX readily etched any glass containers in which it was stored, and the 3 mol-% formal impurity in the FDNE was not eliminated during this preparation. In single trials, compound XIX failed to add either $(EtO)_2MeSiH$, however, or the much more reactive cyclic hydrosilane

$$\left[HSi(Me)O \right]_4$$

used as a model for the desired reaction 11. The hydrosilanes decomposed in both cases as more vigorous heating was applied to stimulate a reaction. This approach to the

$$CH_2{=}CHCH_2NHCH_2CF(NO_2)_2 + (EtO)_2MeSiH \xrightarrow[\Delta]{H_2PtCl_6}\!\!\!\!\!\!/\!/\; XVI \qquad (11)$$

XIX III

aminopropyl (Type B) silicones does not appear promising, especially since one expects the product XVI not to hydrolyze very well to the linear structures probably required for elastomer formation. This anticipated hydrolytic behavior should be confirmed, nevertheless, if possible.

ANALYSIS OF POLYMER PRODUCTS

Section Summary - A key and time-consuming aspect of this year's work has been to develop means of assessing the natures of the polymer precursors and HE product mixtures produced. The relatively uncommon technique of 29-Si-nmr spectroscopy looked particularly promising in view of its usefulness during the HE silane ester phase of our contract work 2 years ago, and we therefore sought to correlate the much smaller chemical shift differences now seen in the present polymer materials with actual siloxane chain structure. Through careful attention to detail and some invaluable literature and in-house reference data on dimethylsilicones, we have succeeded in arriving at the analytical conclusions noted in the previous sections. Thus, linear structures now can be differentiated from cyclic 3,4, and 5-membered ring compounds, and end group Si atoms can be spotted both in the precursor and HE silicone product materials. We are currently working on the resolution of peaks which may correlate to specific locations of Si atoms in the linear chains, but such an advance may be beyond the capability of our already highly sophisticated instrumentation.

Proton nmr spectroscopy has been invaluable in defining the extent of alkylation of amino groups (conversion of FDNE), hydrolysis of ester groups, and presence of impurities.

Molecular weight determinations of some materials have been pursued, since they are clearly necessary to an evaluation of our synthesis products. These measurements have not proved routine, however, as problems of solubility and potential molecular association of polar polymers in non-polar solvents continue to require further resolution and understanding. The values reported probably reflect accurate orders of magnitude, although absolute errors of up to 25% may possibly be involved. From the $M_{\overline{N}}$ values of total samples of mixed linear and cyclic structures, and knowledge of the concentration of each type from the 29-Si- spectra, $M_{\overline{N}}$ estimates of just the linear portions were made.

29-Si-NMR Spectroscopy

The naturally occurring 29-Si isotope in ordinary silicon is magnetic and hence susceptible to nmr detection. Special techniques are necessary, however, to deal with the low natural abundance of 4.7% and problems of long and non-uniform spin relaxation times influenced by interactions with other magnetic nuclei (protons). Our past work on the preparation and analysis of HE silane esters (1) was greatly facilitated by our on-site capability for Fourier transform 29-Si-nmr spectroscopy, and the present work on polymeric materials is even more dependent on this technique.

It was found some time ago that Si atoms absorb at characteristic shifts vs. tetramethylsilane reference depending on the number of alkyl, alkoxy, siloxy, and other groups attached. Within any given general structure, such as (siloxy) $(alkyl)_a$ Si $(alkyl)_b$ (alkoxy), however, further differentiation (fine structure) is possible which reflects differences in the attached groups. Based on past experience with dimethylsilicones and some model (methyl) (aminobutyl) silicones, we have identified characteristic absorptions in the precursor aminoalkylsilicones and their HE derivatives which label the presence of 3, 4, 5, and possibly 6-membered cyclic structures and of linear structures. Some assignments remain to be made, but those which have proved consistent to date have allowed us to define our product mixtures in terms of those polysiloxane backbone units.

Quantitative correlation of peak intensity vs. Si concentration by integration in a difficult and uncertain procedure, however, due to variable spin relaxation effects between the different types of magnetic silicon atoms and protons; these can differently affect the peak intensities of the different 29-Si nuclei when the protons are radiatively decoupled, as is the normal practice. A special decoupling method is therefore used along with an external spin relaxation agent to overcome the slow and variable dependence of the relaxation times and signal strengths on the natural, internal processes. The relaxation additive of choice is Cr $(acetylacetonate)_3$, and estimates of the concentrations of Si atoms according to type have been carried out using this reagent in $CDCl_3$ solvent. Any effect of the Cr complex compared to other spin relaxation agents on the resulting data has not been explored but is probably very minor, since spectra obtained $\pm$ Cr have usually proved highly similar, at least in their major features. Complexation effects in polyamine compounds such as we are dealing with nevertheless remain a potential complication.

From the relative concentrations of Si atoms of various types and knowledge of the structures they represent, one can derive molar concentrations of the species present and calculate from the overall average molecular weight a value for just that portion of the mixture of interest, i.e., the linear species. In our applications of this practice to date, we are carrying an uncertainty factor due to our present inability to distinguish silicons in cyclic structures D''_6 from linear Si atoms at the no. 2 position, i.e., adjacent to terminal SiOH types.

H-NMR Spectroscopy

In addition to the observation of the usual group absorptions for analysis, we have found a clear separation between the region of $>NCH_2CX_3$ and $-OCH_2CX_3$ methylene group absorptions $[CX_3 \equiv CF(NO_2)_2]$. The extent of amino group alkylations by FDNE has therefore been readily defined by observation of the 5.1-4.7 ppm (oxygroup) and 4.0-3.8 ppm (amino group) regions.

Molecular Weight

Number average molecular weights, $M_{\overline{N}}$, have been determined by vapor osmometry for some samples as noted. We are in the process of trying to make such analyses as mutually comparable as possible, but it appears that not all samples will be soluble in the preferred solvent toluene and that considerable variability in the accuracy of the data will be unavoidable. We are currently trying to adapt this otherwise well-refined analytical procedure to the most reliable analysis of the present HE silicone polymers and their precursors.

GELATION OF HE SILICONES

Summary and Results - Some preliminary studies have been carried out in the HE-aminobutyl silicone system in order to assess the potential for chain extending the HO-ended linear units to high $M_{\overline{N}}$ structures with elastomeric properties. Neat samples of the HE silicone XIII prepared from the 75% linear aminobutylsilicone were treated with 1 vs. 0.5 mole of chain extender silanes per equivalent of SiOH (calculated for the average structure $HOD''_{34}H$). Gelation without apparent decomposition occurred at room temperature or 55°C in the presence of $MeSi(OAc)_3$. Amino reagents required 55° but accelerated sample decomposition *vs. alkoxysilanes. At 80° both* treated and untreated samples decomposed with the slow liberation of a gas to leave a flexible foam; the gas had an odor similar to that of a low molecular weight hydrocarbon. The decomposition was reminiscent of that observed to varying extents in the HE ethylenediaminopropyl system at room temperature.

More complete blocking of basic amino groups in future HE silicone products may enhance the stability considerably. We shall shortly examine the decomposition reaction in more detail to identify the gaseous species liberated and gain a clue to countering the process. Chain extensions with oxy- rather than amino-ligand silanes will be emphasized.

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