Exactly Alternating Silarylene–Siloxane Polymers. I. The Synthesis and Stability of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane

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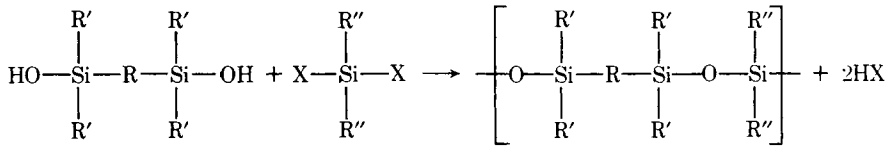
Synopsis

Ureidosilanes have been found to be active monomers for the preparation of siloxane polymers by step-growth polymerization reactions at low temperatures. For this purpose, very high monomer purities are required, and the present investigation was concerned with the purity and stability of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane prepared from the diaminosilane and phenyl isocyanate. Preparation of the monomer by this reaction at −20°C gave directly a product of very high purity suitable for the preparation of very high molecular weight polymers. Pseudo-first-order rate constants were obtained on the hydrolysis of the monomer during synthesis and storage.

INTRODUCTION

Linear, high molecular weight polymers containing siloxane repeating units are normally prepared by the ring-opening polymerization reactions of cyclic siloxane monomers with ionic initiators. This type of reaction is a chain-growth polymerization, and high molecular weight polymers are readily obtained. However, it has become increasingly of interest to prepare organosiloxane polymers containing arylene units within the backbone of the main chain, and for this purpose condensation or step-growth polymerization reactions must be used. Most such polymerization reactions have been based on the condensation of a silanol monomer with an active silane monomer through a nucleophilic substitution reaction, as follows:



A number of active silane monomers have been investigated for this purpose with different leaving groups X, particularly the dialkylamine[1] and acetoxy groups.[2] With both of these specific leaving groups, the by-product from the reaction is a reactive compound (a basic secondary amine or an acidic carboxylic acid, respectively), and these compounds can cause acid- or base-catalyzed chain cleavage reactions in siloxane polymers, thereby creating problems in preparing high molecular weight products.

There has been considerable interest in the use of active silane monomers containing leaving groups which would form unreactive by-products in the polymerization reaction. A particularly interesting example of such a derivative

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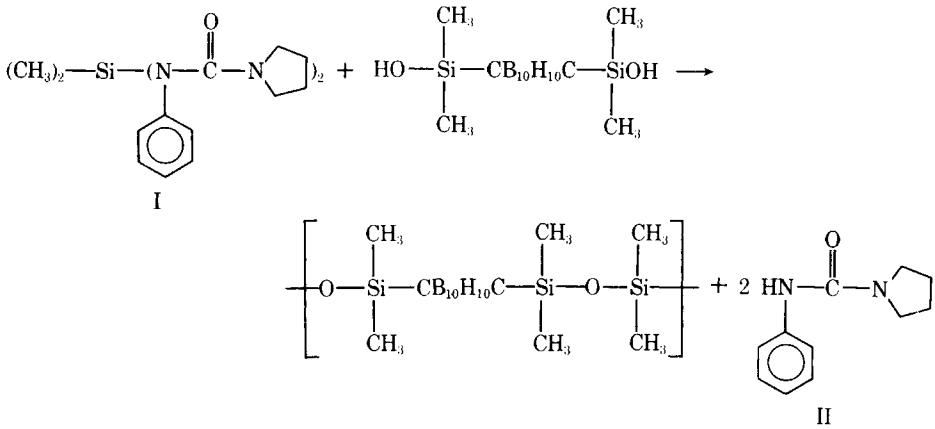
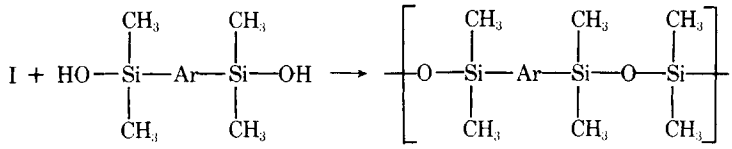
is the N,N-dialkyl-N′-phenylureidosilane, which has been used for the preparation of high molecular weight carborane–siloxane polymers by the condensation polymerization reaction of a difunctional silane monomer of this structure with a carboranedisilanol monomer.[3] The specific active silane monomer used was bis(1,1-tetramethylene-3-phenylureido)dimethylsilane (I), and the by-product of this reaction is a neutral, presumably unreactive compound, 1,1-tetramethylene-3-phenylurea (II), as follows:



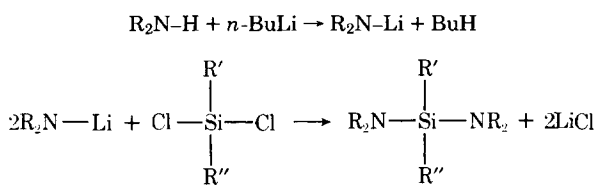
This type of reaction is being applied in our laboratory for the preparation of exactly alternating silarylene–siloxane polymers for thermally stable elastomers from arylene disilanols as follows:



PREPARATION OF BISUREIDOSILANE MONOMER

The general synthetic procedure for the preparation of bis(1,1-dialkyl-3-phenylureido)silanes was reported by Hedaya and co-workers.[3] Of the various derivatives described, the bis-1,1-tetramethylene derivative (I) was found to be the easiest to prepare in the purest state because of its ease of crystallization from the reaction mixture. However, even this derivative was not obtainable completely pure because it was always contaminated with 1,1-tetramethylene-3-phenylurea (II).

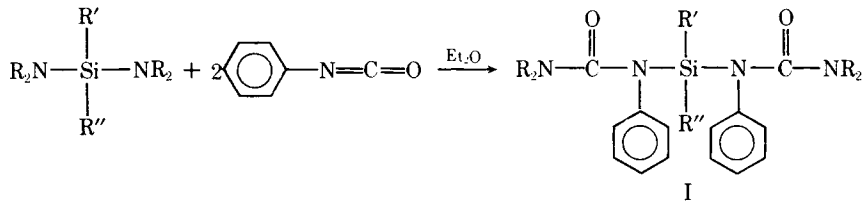
In order to prepare the bisureidosilane monomer (I) in as high purity as possible, the synthetic reaction conditions were examined in detail in the present investigation. The procedure used was that described by Hedaya and co-workers which started with the preparation of a silylamine from the corresponding dichlorosilanes, as follows[3]:



$$R_2N\text{-}H + n\text{-}BuLi \rightarrow R_2N\text{-}Li + BuH \quad (1)$$

$$2R_2N\text{—}Li + Cl\text{—}Si(R')(R'')\text{—}Cl \rightarrow R_2N\text{—}Si(R')(R'')\text{—}NR_2 + 2LiCl \quad (2)$$

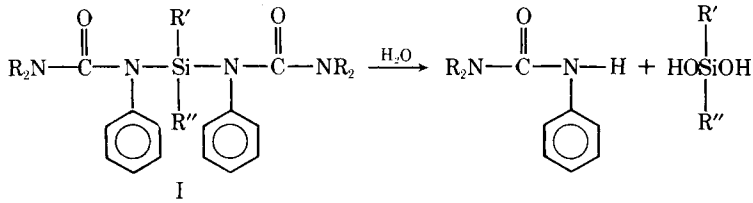
The amino derivative was converted into the bisureidosilanes (I) by an insertion reaction of phenyl isocyanate into the silicon–nitrogen bond, as follows:



(3)

This step was performed in diethyl ether solution in which the bisureidosilane monomer was insoluble and could be readily isolated by filtration.

Bisureidosilanes are known to be very reactive toward proton-donating agents, which readily attack the Si–N bond. This type of reactivity makes these compounds very reactive to traces of water to form the corresponding unsymmetrical urea:



(4)

The urea obtained was poorly soluble in diethyl ether, and it precipitated out of the reaction mixture, contaminating the monomer formed. Consequently, only in an absolutely dry reaction medium could pure bisureidosilane be prepared at room temperature and above, and this degree of drying was not achieved in conventionally dried solvents.[4]

To determine the purity of the bisureidosilanes prepared, as well as to follow the purification methods which were attempted, proton NMR spectroscopy was used to analyze the reagents and the products. Two approaches were investigated to prepare pure compounds; these were (1) purification of the urea-contaminated products and (2) optimization of the conditions employed in the insertion reaction (3).

EXPERIMENTAL

Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane

Bis(tetramethyleneamino)dimethylsilane was prepared according to the general procedure described in the literature.[3] Phenyl isocyanate was purified by vacuum distillation, and the fraction boiling at 30°C at 0.6 mm was used in the reaction. Diethyl ether was dried by distillation from *n*-butyllithium.

Dry diethyl ether (500 ml) was placed in a 1-liter, three-necked flask equipped with a mechanical stirrer, dry ice condenser, and thermometer and maintained under nitrogen atmosphere. The apparatus was very carefully heated under vacuum and purged with dry nitrogen several times before ether was added. Bis(tetramethyleneamino)dimethylsilane (81.6 g, 0.411 mole) was added to the solvent and the mixture was well stirred and cooled to the desired reaction temperature. Under a strong nitrogen purge, a dropping funnel containing 89.4

TABLE I
NMR Shift Assignments for Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane (I) and 1,1-Tetramethylene-3-phenylurea (II)[a]

Compound	Si—CH_3	(—CH_2—)$_2$	Chemical shift, ppm[b] (—CH_2—N—CH_2—)	N—H	Aromatic
I	0.98, s.	1.80, quin.	3.40, t.		7.20–8.00, mult.
II		1.98, quin.	3.65, t.	7.05, s. (broad)	

[a] s., singlet; quin., quintuplet; t., triplet; mult., multiplet.
[b] In deuterated chloroform.

ml (0.823 mole; 98.0 g) of freshly distilled phenyl isocyanate was attached to the reaction flask and the isocyanate was added dropwise. At the end of the addition, a white precipitate of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane appeared. When the concentration of the reaction solution was decreased, the precipitate would not form right away but would appear after overnight stirring of the reaction mixture.

The reaction mixture was filtered under an inert atmosphere using a sintered-glass funnel to yield 153.1 g (85.4%) of crude bisureidosilane. The product was washed with 1.5 liter dry diethyl ether and dried at room temperature under vacuum at 0.6 mm Hg for 48 hr.

The product's NMR spectrum, obtained with a 90 MHz Perkin–Elmer proton NMR spectrometer, model R-32, was used to determine the purity of the product. Solutions in deuterochloroform were prepared in an inert atmosphere of prepurified nitrogen and were sealed in tubes. The peak assignments for the NMR spectra of pure bis(1,1-tetramethylene-3-phenylureido)dimethylsilane and 1,1-tetramethylene-3-phenylurea (obtained by hydrolysis of the former by water) are listed in Table I.

Monomer Stability

NMR spectroscopy was also used to study the effect of storage conditions on monomer stability. In each of the experiments, 5 g of urea-free bisureidosilane was placed within a dry bag filled with nitrogen into a 50-ml one-necked, round-bottomed flask and the samples were exposed to the following conditions: (1) air at room temperature (open flask on a bench top); (2) vacuum at −5°C (evacuated flask in a refrigerator); (3) nitrogen at room temperature (in a nitrogen-filled desiccator); and (4) nitrogen at −20°C (under nitrogen atmosphere stored in a freezer).

During the initial stages of the experiments, samples were taken every day and analyzed for their urea content by NMR spectroscopy. Later it was done at weekly intervals.

With the exception of the sample of bisureidosilane exposed to air, all solutions for proton NMR analysis were prepared in a dry bag under nitrogen atmosphere. The solid compound was dissolved in deuterated chloroform and injected into an NMR tube filled with nitrogen and the tube was carefully sealed. The amount of urea formed on storage was determined by integration of the peaks at $\delta = 1.98$ ppm and $\delta = 3.65$ ppm for urea and the peaks at $\delta = 1.80$ ppm and $\delta = 3.40$ ppm for bisureidosilane.

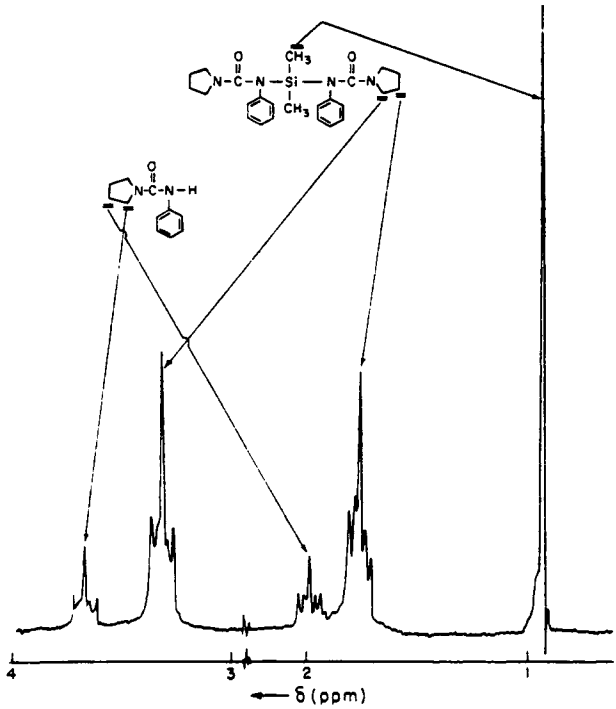


Fig. 1. Typical proton NMR spectrum of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane contaminated with 1,1-tetramethylene-3-phenylurea in deuterated chloroform.

RESULTS AND DISCUSSION

The presence of small amounts of urea impurity, II, in monomer I could be readily determined by proton NMR spectroscopy because the chemical shifts of the methyl and pyrrolidinyl groups are considerably different in the two compounds. Hence, a typical spectrum for a sample of monomer contaminated with II is shown in Figure 1. The peak area measurements of the spectrum of Figure 1 indicate that the monomer, in this case, was contaminated with almost 30% of the impurity II.

Several procedures were examined in the present study for the purification of the monomer, including the following: (1) extraction of II with diethyl ether under dry nitrogen, (2) recrystallization of the monomer from a tetrahydrofuran solution by dropwise addition of diethyl ether, (3) recrystallization of the monomer from a chloroform solution by slow cooling, and (4) selective extraction of the monomer by chlorobenzene. Unfortunately, none of these procedures was found to be of practical use. The first two led to a monomer contaminated with 5–10 mole % urea at best, most probably because of insufficient dryness of the ether solvent, which was dried according to the usual procedures. The other two methods proved to be unsatisfactory for handling large quantities of the monomer because of its high degree of solubility in both solvents. However, very pure monomer was obtained by the first two procedures when the ether was distilled under nitrogen from an n-butyllithium solution directly into the flask containing the bisureidosilane.

TABLE II
Effect of Insertion Reaction Temperature on Monomer Purity

Reaction conditions		Silylamine[a]		Phenyl isocyanate		Diethyl		Monomer
Temp., °C	Time, hr	g	mmole	g	mmole	ether, ml	Yield, %	purity, %[b]
0	1	9.924	50.12	11.909	100.08	50.0	83.2	68
−5	1	9.882	49.93	11.905	100.04	50.0	84.6	89.5
−10	1	9.906	50.03	11.914	100.12	50.0	85.8	95.5
−21	1	9.853	49.76	11.769	98.90	50.0	85.0	99
−28	1	9.910	50.05	11.905	100.04	50.0	85.4	100

[a] Bis(tetramethyleneamino)dimethylsilane, compound I.
[b] Mole % monomer in precipitated product; remainder is urea impurity as determined by NMR analysis.

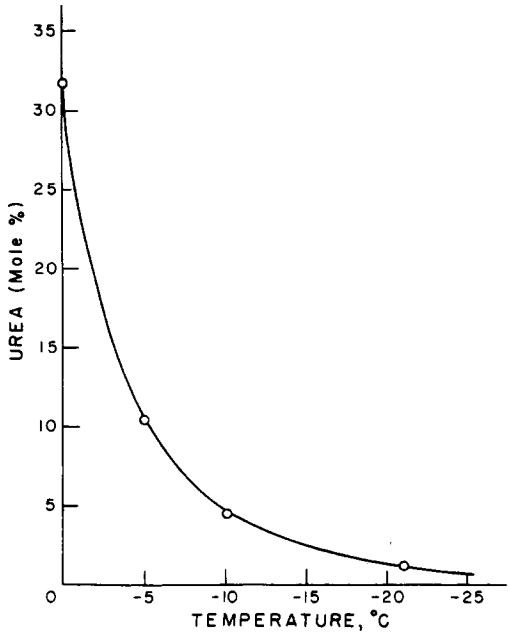


Fig. 2. Effect of reaction temperature on amount of urea contaminant formed in the insertion reaction.

Effect of Reaction Temperature

Bis(tetramethyleneamino)dimethysilane, which was reacted with phenyl isocyanate in reaction (5), is a liquid which boils at 58–60°C at 0.6 mm Hg, and it can be obtained in high purity by careful vacuum distillation from the mixture resulting from reaction (2). The insertion reaction is believed to be the purity-controlling step in the synthesis of the bisureidosilanes, and there were strong indications that the use of the incompletely dried solvent in this reaction was the likely source of water, which reacted with the monomer after its formation by reaction(4) to produce the urea impurity. If so, it was thought that the use of a lower reaction temperature would decrease the rate of this side reaction and favor the preparation of the bisureidosilane in high purity.

To determine the effect of reaction temperature on product purity, a series of reactions was run at temperatures ranging from 0 to −30°C, as described in Table II. Reaction times of 1 hr each were used at all temperatures starting from the addition of phenyl isocyanate into a bis(tetramethyleneamino)dimethylsilane solution and continuing until the product was filtered. The purity of the products was determined by NMR spectroscopy with the results collected in Table II. The amount of urea contaminant present in the monomer is plotted as a function of reaction temperature in Figure 2.

The results showed that purity of the monomer was very sensitive to the temperature at which phenyl isocyanate was inserted into the Si–N bond of the silyldiamine in reaction (3). It was found that the purity increased with decreasing reaction temperature, and for practical purposes a minimum reaction temperature of −20°C was required to prepare highly pure monomer. Apparently, at this temperature the hydrolysis reaction is very slow, and the monomer

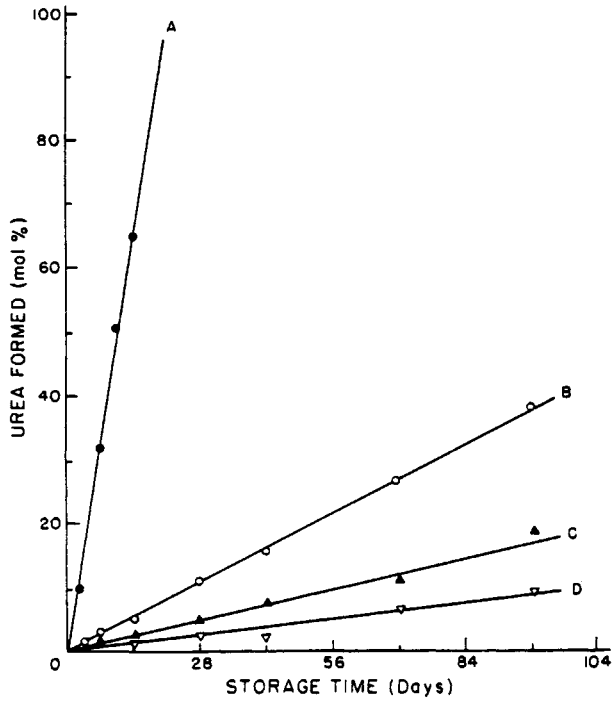


Fig. 3. Formation of urea contaminant in monomer under the following storage conditions: (A) air at room temperature; (B) vacuum at −5°C; (C) nitrogen at room temperature; and (D) nitrogen at −20°C.

can be formed and isolated by the insertion reaction with little or no urea formation.

Monomer Stability

It had been observed in all previous polymerization studies that storage of the monomer under a wide variety of conditions invariably led to formation of and contamination by the unsymmetrical urea. To determine the extent of monomer instability, the following storage conditions were examined for the formation of II as a function of time: (1) storage in air at room temperature, (2) storage under vacuum at −5°C, (3) storage under dry nitrogen at room temperature maintaining a slightly positive nitrogen pressure over the sample, and (4) storage under dry nitrogen at −20°C under a positive nitrogen pressure. In each case samples were removed daily and examined for purity by NMR spectroscopy. Considerable care was used to transfer the sample under a dry nitrogen atmosphere into the NMR tube. The results for the conversion of monomer to urea contaminant as a function of time under these conditions are collected in Table III and plotted in Figure 3.

On the basis of these data, calculations indicated that the conversion of the bisureidosilane monomer to the urea contaminant followed pseudo-first-order kinetics as indicated by the conversion–time plots in Figure 4. The reaction involved is presumably hydrolysis of the monomer by adventitious water, which enters the system during storage, as shown in the following equation:

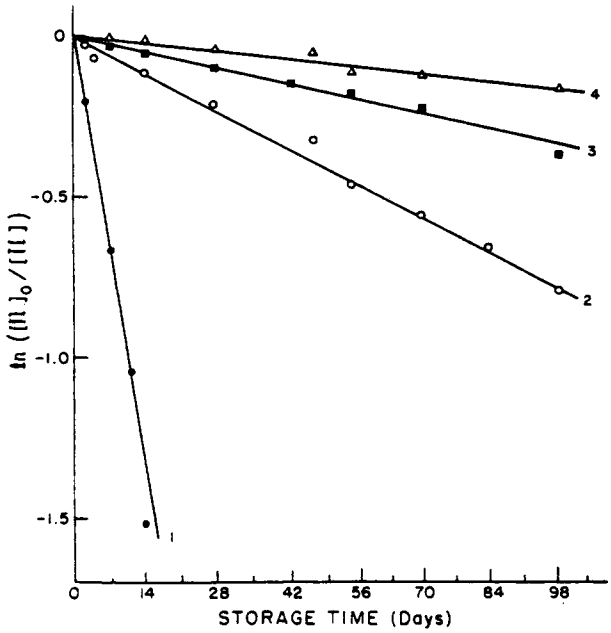
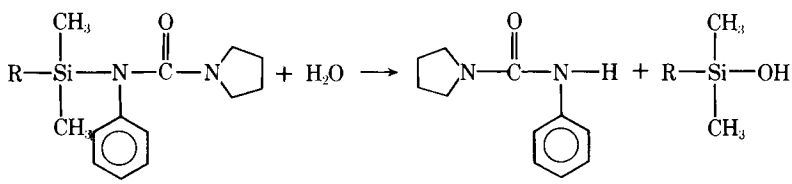


Fig. 4. First-order rate plots for monomer hydrolysis under the following storage conditons: (1) air at room temperature; (2) vacuum at −5°C; (3) nitrogen at room temperature; and (4) nitrogen at −20°C.



(5)

According to this reaction, each partially reacted molecule of bisureidosilane would yield one molecule of urea. The general rate expression for reaction (5) is

$$-\frac{d[\mathrm{I}]}{dt} = k[\mathrm{I}][\mathrm{H_2O}] \tag{6}$$

If the water concentration was kept constant in the system, or if it was either too large or too small compared to the concentration of the bisureidosilane, an apparent first-order rate constant k' could be calculated as follows:

$$k' = k[\mathrm{H_2O}] \tag{7}$$

$$-\frac{d[\mathrm{I}]}{dt} = k'[\mathrm{I}] \tag{8}$$

Plots of ln $([\mathrm{I}]_0/[\mathrm{I}])$ as a function of time for each of the storage conditions are given in Figure 4. These plots show a relatively good straight-line behavior. The apparent first-order rate constants were calculated for each set of storage conditions, and the data for a typical determination is shown in Table IV. The average values for the constants obtained at each set of storage conditions are summarized in Table V.

TABLE III
Amount of Urea Contaminant Formed Under Different Monomer Storage Conditions

Time, days	Urea content in monomer sample, mole%			
	Air at room temp.	Vacuum at −5°C	N_2 at room temp.	N_2 at 20°C
3	10	1.5	—	—
7	32	3.5	1.5	0.5
11	50	—	—	—
14	64	5.5	3	1
28		10.5	5	2
42		—	7.5	—
48		16	—	2.5
56		23	9	6
70		27	11.5	6.5
84		32	—	—
98		38	19	9

TABLE IV
Apparent First-Order Rate Constants for Monomer Hydrolysis at −5°C Under Vacuum

Peak area ratios[a]	mole %	Time, days	$\ln [I]_0/[I]$	$k' \times 10^3$, days^{-1}
0/100	100	0		
1.5/98.5	97.0	3	0.030	10.0
3.5/96.5	93.2	7	0.069	9.9
5.5/94.5	89.6	14	0.110	7.9
10.5/89.5	81.0	28	0.211	7.5
16/84	72.4	48	0.323	6.7
23/77	62.6	56	0.468	8.4
27/73	57.5	70	0.554	7.9
32/68	51.5	84	0.663	7.9
38/62	44.9	98	0.800	8.2
Average				8.1

[a] Ratio of integrated areas of urea and monomer peaks in the NMR spectrum of the sample after storage.

TABLE V
Average Apparent First-Order Rate Constants for the Hydrolysis of Bis(1,1-tetramethylene-3-phenylureido)dimethylsilane Under Various Storage Conditions

Atmosphere	Temp., °C	k', days^{-1}
Air	room	9.3×10^{-2}
Vacuum	−5	8.1×10^{-3}
Nitrogen	room	3.7×10^{-3}
Nitrogen	−20	1.7×10^{-3}

It is apparent from the results that the rate of hydrolysis of the monomer, when exposed to normal atmospheric moisture, was quite high, and substantial contamination with the urea occurred in a relatively short period of time. The results for the decomposition under dry nitrogen at room temperature and at −20°C may suggest that the activation energy for conversion of I to II is quite high because an increase in temperature of approximately 40°C caused only an approximately twofold increase in the rate of decomposition. On the other hand, the apparent rate constant contains a term for the concentration of water in the

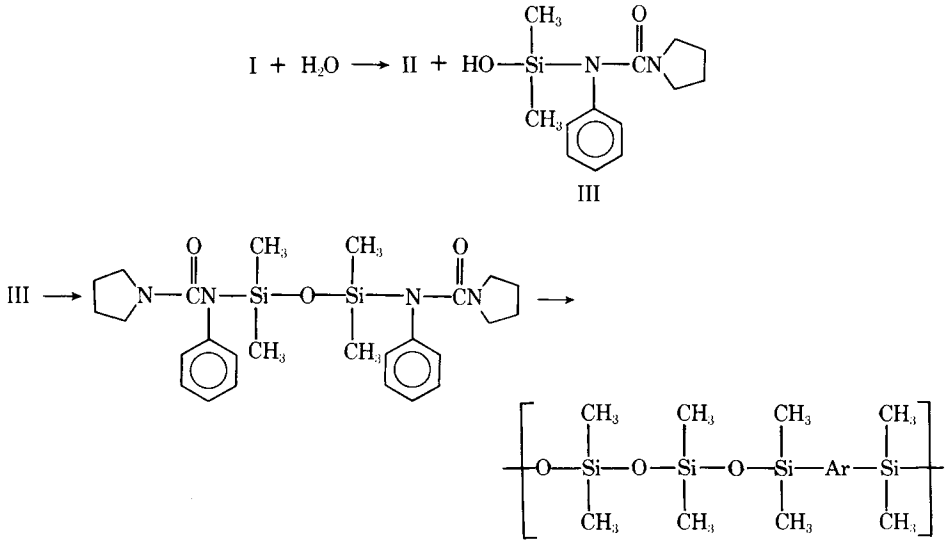
storage environment, and the difference observed may just be an indication of a lower constant water concentration at the lower storage temperature.

The results for the decomposition under vacuum at −5°C were not consistent with the nitrogen atmosphere results. A possible explanation of this discrepancy would be that the samples maintained under vacuum were exposed to a higher concentration of water than those maintained under dry nitrogen.

CONCLUSIONS

This investigation has shown that the temperature used for the preparation and storage of the ureidosilane monomer I was the most important factor in obtaining the type of high-purity monomer which is required for the preparation of high molecular weight polymer by a step-growth polymerization reaction. The phenylurea contaminant II was not in itself a problem in the use of the monomer for the polymerization reaction because it was unreactive and was formed as a by-product, in any case. But the extent to which it was present in the monomer was difficult to measure exactly, and this uncertainty created problems in obtaining an exact equivalence of the two monomers for the polymerization reaction.

The presence of II also implied that a hydroxydimethylsilane group was present to the same extent as the urea formed in the monomer (assuming II was formed by the hydrolysis of I) and, hence, it was also available as a coreactant in the polymerization. The presence of this hydroxysilane group would create two problems: first, it would exaggerate the functional group imbalance; and secondly, it could lead to the formation of disiloxane units in the polymer formed as shown in the reaction below. Such units would represent undesirable structures because they could serve as sites of thermal and chemical instability in the silarylene–siloxane polymers.



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