

STUDIES ON THE POLYSILANE CONSISTING CYCLODISILAZANE UNITS IN THE MAIN CHAIN

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ABSTRACT

Since the reactivity of Me_2SiCl_2 (I) and $\text{Cl}-\text{Si}(\text{Me})_2-\text{N}(\text{Me})_2-\text{Si}(\text{Me})_2-\text{N}(\text{Me})_2-\text{Si}(\text{Me})_2-\text{Cl}$ (II) are very different,

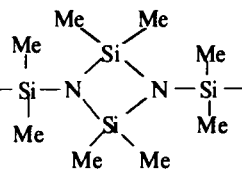
it is difficult to cocondensate the above two monomers with sodium in general Wurtz reaction. We have proposed a modified method to prepare copolymer containing permethylpolysilane segments and cyclodisilazane units by reaction of (II) with Na at first, then adding (I) into the mixture to proceed with further reaction.

The obtained copolysilanes are pale yellow elastic substance and soluble in common solvents. The amounts of N in the copolymers are influenced by the operating conditions of the synthetic method. The resultant products were characterized by IR, UV, NMR, and elementary analysis. The highest molecular weight determined by gel permeation chromatography is 60000.

INTRODUCTION

The first organosilane polymers based on diphenylsilane units were synthesized by Kipping in 1924^[1] and permethylpolysilane was prepared by Burkhard in 1949^[2]. Both polymers were, however, high crystalline, intractable white powders which decomposed under heating. Recently, there has been a resurgence of interest in organosilane polymers and copolymers used as precursors for $\beta-\text{Si}-\text{C}$ fibers^[3, 9-11], as impregnating agents for strengthening ceramics^[8] and as dopable semiconductors^[11]. For these purposes many investigators have synthesized a lot of organosilane homopolymers and copolymers, which are soluble in common organic solvent and can be molded or drawn into fibers^[9-11]. But up to now, no paper has reported about the synthesis of polysilane consisting of cyclic moiety with N in the main chain. We now

have synthesized a series of polysilanes containing disilazane ring



in it.

The properties and structures have been characterized.

EXPERIMENTAL

1. Raw materials

Dimethyldichlorosilane was purified by rectification, B.P. 70.5 °C, purity was: 99.5%.

(II) was synthesized by Fink's method^[4]. The melting point and the H_1 NMR are in agreement with that of the reference^[5]. Toluene was dried by refluxing over Na wire.

2. Copolymerization

An example was (I) : (II) = 10 : 1. The others were with similar process.

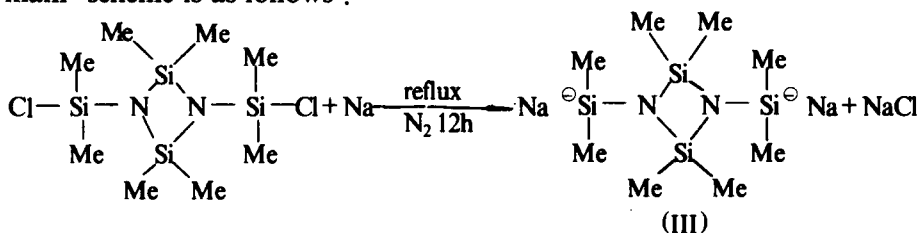
A 250 ml three-necked round bottom flask was fitted with a reflux condenser drop funnel and a stirrer. The equipment was thoroughly dried and purged with nitrogen. Care should be taken to avoid light from the reaction mixture. To the reaction flask were added 20ml toluene and 1.01 g(0.044mol) sodium under N_2 . Then, this was heated to gentle reflux and started vigorous stirring. The toluene solution of [II] (0.02 mol of [II] in 15 ml of toluene) was added dropwise to the vigorously stirred mixture in 15 — 20 min and refluxing continued till the solution became neutral. Now, 0.2mol dimethyldichlorosilane was added dropwise to the flask and refluxing was continued for six hours. The solution became deep violet. More sodium (10.1g, 0.44mol) was added and refluxing again for another six hours. The hot reaction mixture was cooled to room temperature and filtered. To the filtrate was added 80 ml methanol and pale yellow copolymer was isolated. Then the copolymer was dried in vacuum oven, 7.4 g pale yellow colloidal polymer was obtained. 50 ml ethanol was added to the remained solid residue to decompose the rest sodium. NaCl was removed by washing with water. 2.2g insoluble permethylpolysilane was recovered from the residue.

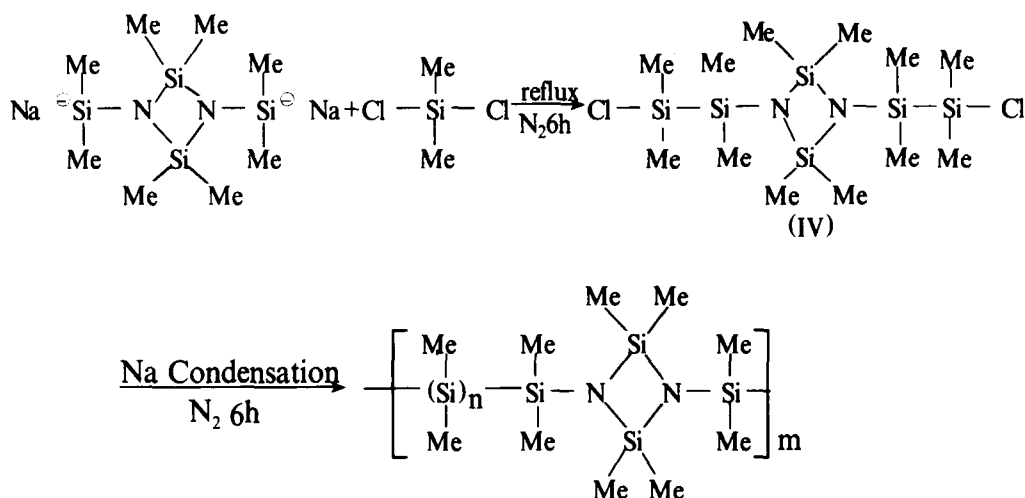
RESULTS AND DISCUSSION

1. Selection of synthetic methods

The reactivity of [I] is much higher than that of [II]. When the toluene solution of [I] and [II] was refluxed over sodium for 12 hours no soluble polymer was formed, except that insoluble intractable white powder was obtained, which was homopolymer of [I]. When [II] was refluxed in the same condition homopolymer of [II] could not be obtained so that polymers obtained by using step polymerization are copolymer of [I] and [II].

The main scheme is as follows :





The excess of Na was added to promote the formation of [III] which then condensed with [I]. As soon as [IV] formed, its reactive terminal Si—Cl bond would easily react with Na forming new Si anion. In this manner polymerization would proceed smoothly. Because the end Si atom of [II] links directly to the N atom and the lone electron pair of N conjugates to the 3d orbitals of Si, it is difficult to form Si anion. If [III] formed it reacted with [I] to form [IV], that is, the end Si atom links to another Si atom and the influence of N atom on the end Si atom is decreased. The condensation activity is increased.

2. Effects of reaction condition

It is well known that Si—N bond is easy to be alcoholized and hydrolyzed in base environment, so it is necessary to avoid the polymer getting in touch with alcohol under the existence of base during separation from reaction solution by methanol and isopropanol, or the Si—N bond would be decomposed. Because of this, before the polymer was deposited from solution by alcohol, the filtration of the rest sodium should be performed first. Thus the polymer was separated from the basic system and deposited in neutral condition. It has been proved that if the polymer was treated in common way, the Si—N bond would be broken into volatile NH_3 .

3. Elementary analysis

We have synthesized a series of copolymers with various ratios of [II] : [I]. The data of elementary analysis of corresponding polymers are shown in Table 1.

Table 1 Elementary analysis of the copolymers

[II] : [I]	1:10	1:5	1:2	1:1
Amount of N %	2.20	4.19	6.00	7.92
Theoretical amount of N %	3.3	5.1	7.45	8.8

From the elementary analysis data about 60% of N were increased in the copolymer. These results illustrated that this synthetic method was very available.

4. Pyrolytic gas chromatography

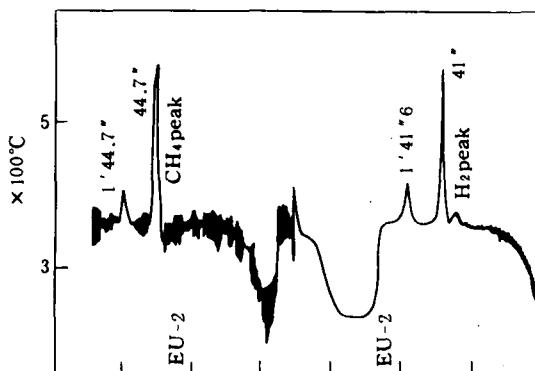


Fig. 1 Pyrolytic gas chromatograph of copolymers

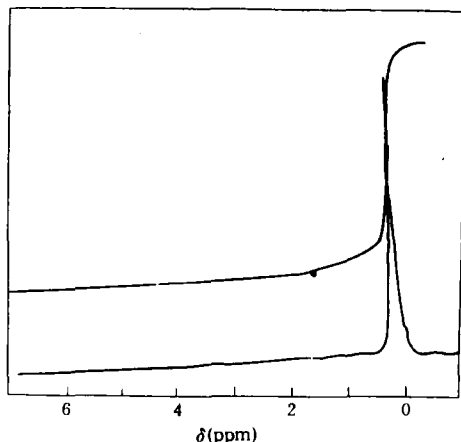
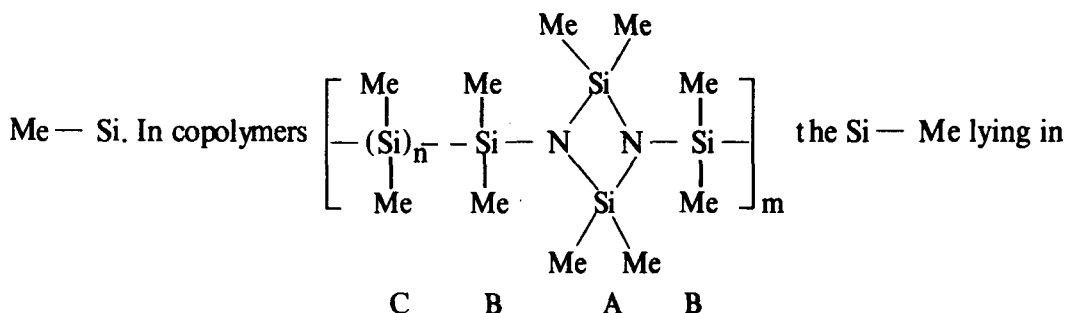


Fig. 2 H^1 NMR spectra of copolymers

The evolved gases were determined by pyrolytic gas chromatography. Only H_2 and CH_4 could be detected. No volatile nitrogen compound was found. This showed that disilazane ring was stable at $700^\circ C$.

5. H^1 NMR Spectra.

The absorptions between $-2.0 - 0.4$ attributed to three kinds protons of



(A) was effected by the tension of the ring and the two N atoms. Its chemical shifts were $0.4 \text{ ppm}^{[6]}$. The Si — Me lying in (B) was effected by only one N atom, its chemical shift was about 0.2 ppm . The Si — Me lying in (C) was effected neither by N atom nor by the tension of the ring, its chemical shift was about 0 ppm . The three kinds of Si — Me protons couple would produce a wide absorption peak.

6. IR spectra

In IR spectra, the C—H absorption is at $2985, 1485, 1253$. von Hans Burger studied the IR spectra of [II] in 1966. He listed the characteristic IR absorption of [II] and Si — N — H^[7]. The IR absorptions of copolymers were in agreement with that listed. The IR absorptions of Si — N — H and N — H are not found (see Table.2). This proves that disilazane ring is stable in our reaction condition.

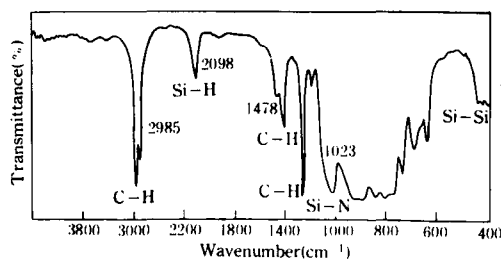


Fig. 3 IR spectra of copolymers

Table. 2 The IR absorption of copolymers and [II]

Bond	Si—N						Si—N—H	N—H
Reference value(cm^{-1})	1025 — 1045	877 — 902	768 — 780	475 — 780	692 — 722	424 — 437	1190	3500
Copolymer(cm^{-1})	1023	881	783	484	728	432	No	No
Polycarbosilane(cm^{-1})	1025	880 902	770		699		No	No

7. UV spectra.

The ultraviolet spectra of copolymers prepared with various ratios of [II]: [I] are

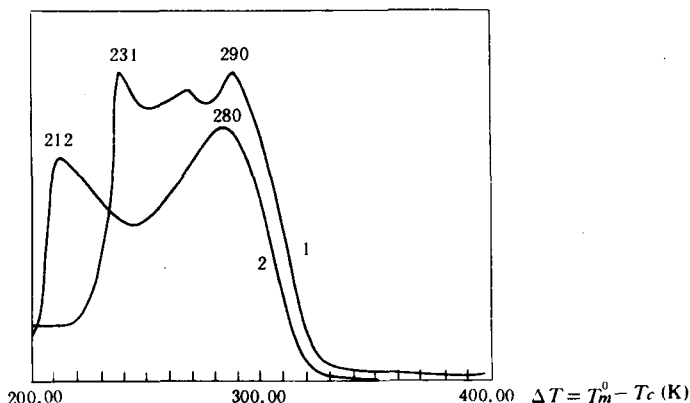


Fig. 4 The UV spectra of copolymers

1) Si—N: Me_2SiCl_2 = 1:10 ; 2) Si—N: Me_2SiCl_2 = 1 : 5

shown in Fig. 4. All of the copolymers have absorption bands in near ultraviolet region which attributed to their silicon framework. With the increasing of disilazane ring in the copolymer an obviously hypsochromic shift was observed, This was due to that the disilazane moiety was non-planar. When this moiety inserted into this polysilane chain, the chain would become noncontinuous owing to the (d—d) conjugation being destroyed. The excited state energy would become higher.

8. The thermal decomposition from polysilanes to polycarbosilanes

Polysilane containing disilazane rings was thermally treated 2 hours in nitrogen at 350 °C, a deep yellow sticky material was obtained. This sticky material was soluble in common solvent such as toluene, CHCl_3 , THF. After thermal decomposition the

characteristic absorption of Si—H at 2098 in IR spectra appeared, the characteristic absorption peak of disilazane ring remained. This illustrated that disilazane ring was stable at this severe condition.

The IR spectra after thermal decomposition are shown in Fig. 5.

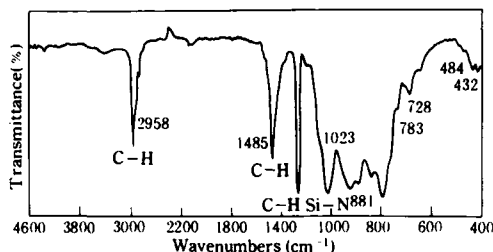
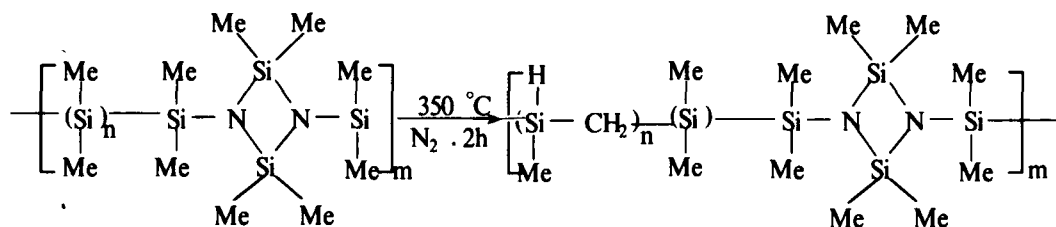


Fig. 5 IR spectra after thermal decomposition

The possible mechanism of thermal decomposition is as follows:



9. Property of the copolymers.

These copolymers are pale yellow elastic material at room temperature and can be molded or drawn into fibers. The soft point is listed in Table 3. They can be dissolved completely in benzene, toluene, THF, CHCl_3 etc.

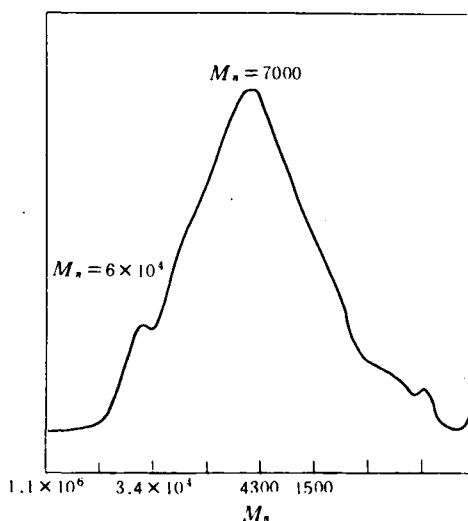


Fig. 6 The G.P.C curve of copolymer.

Since the copolymers have good thermostability, we may conjecture that the

copolymers will be a good material for producing β — Si— C, Si_3N_4 fibers having heat resistance property.

The G.P.C curve of copolymers is shown in Fig. 6.

Table 3 The soft point of copolymers

[I] : [II]	10 : 1	5 : 1	2 : 1	1 : 1
Soft point (°C)	58 ~ 75	162 ~ 198	222	250

Keywords :

Cyclodisilazane ; Polysilane ; Polycarbosilanes

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