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POLYCARBOSILANES - AN OVERVIEW

by

Dietmar Seyferth



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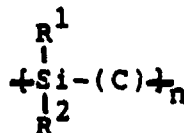
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POLYCARBOSILANES: AN OVERVIEW

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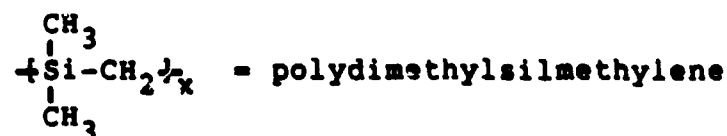
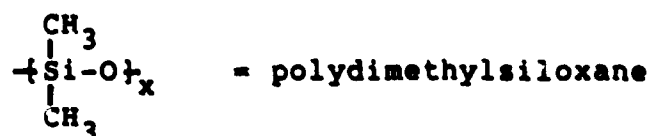
Polycarbosilanes, in their broadest definition, are organosilicon polymers whose backbone is composed of silicon atoms, appropriately substituted, and difunctional organic groups which bridge the silicon atoms, as shown in formula 1. The polycarbosilanes may be linear, or they can be cyclic or polycyclic,



1

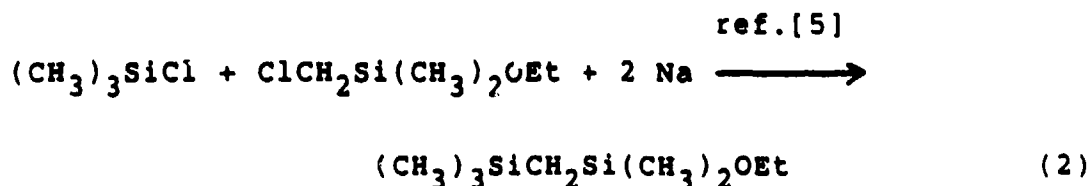
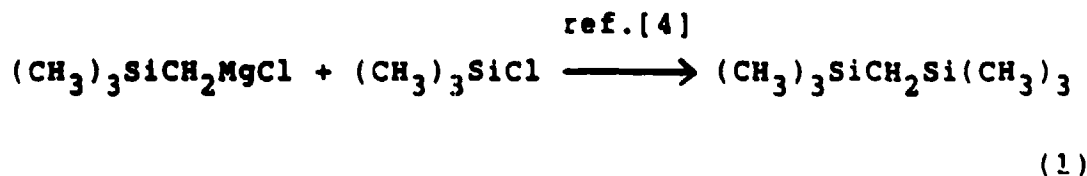
Or they can be hybrids of two or all three of these. The organic "bridge", -(C)-, can be quite varied - a patent attorney's delight: CH₂, CH₂CH₂, higher (CH₂)_n (>3), CH=CH, CH₂CH=CHCH₂, C≡C, CH₂C≡CCH₂, arylene, xylylene, etc., etc. We shall restrict the scope of this discussion to the case where the connecting bridge is CH₂, i.e., the "polysilmethylenes". since a

major emphasis will be on polymeric precursors for silicon carbide, i.e., on carbosilane-type preceramic polymers [1] whose pyrolysis gives a ceramic product as close as possible to the composition SiC. The polysilmethylenes may be viewed as the carbon analogs of the polysiloxanes:



Carbosilanes, defined this narrowly, as a class, monomers, cyclic and polycyclic oligomers and linear polymers, with emphasis on the cyclic and polycyclic systems, have been discussed in detail in an excellent recent book by Fritz and Matern [2].

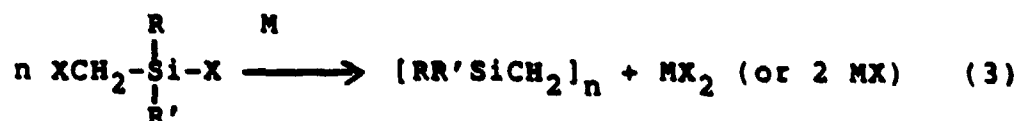
The possibility of linear polysilmethylenes (although none were known at the time) was discussed by Rochow in his seminal book on organosilicon chemistry in 1949 [3]. At that time, two of the applicable preparative procedures had been reported, but had, as yet, only been applied to "small" molecules (eq. 1 and 2). Goodwin and Clark at Dow Corning Corporation



prepared lower oligomers containing at least three silicon atoms by

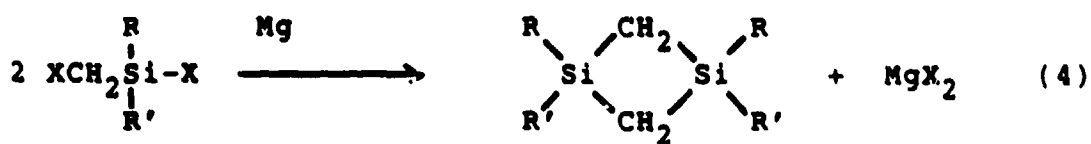
organomagnesium, organosodium or organoaluminum routes [6] and Sommer, Mitch and Goldberg [7] using an organolithium route, prepared methylpolysilmethylenes, $\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{CH}_2]_n\text{H}$, with $n = 2, 3, 4, 5$. These stepwise procedures, however, were not readily applicable to the synthesis of polysilmethylenes of higher molecular weight.

It was the action of reactive metals on (halomethyl)halosilanes (eq. 3) which provided a general route to such polymers. Thus, the action of sodium on $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ gave $[(\text{CH}_3)_2\text{SiCH}_2]_n$ [8]. Removal of a volatile



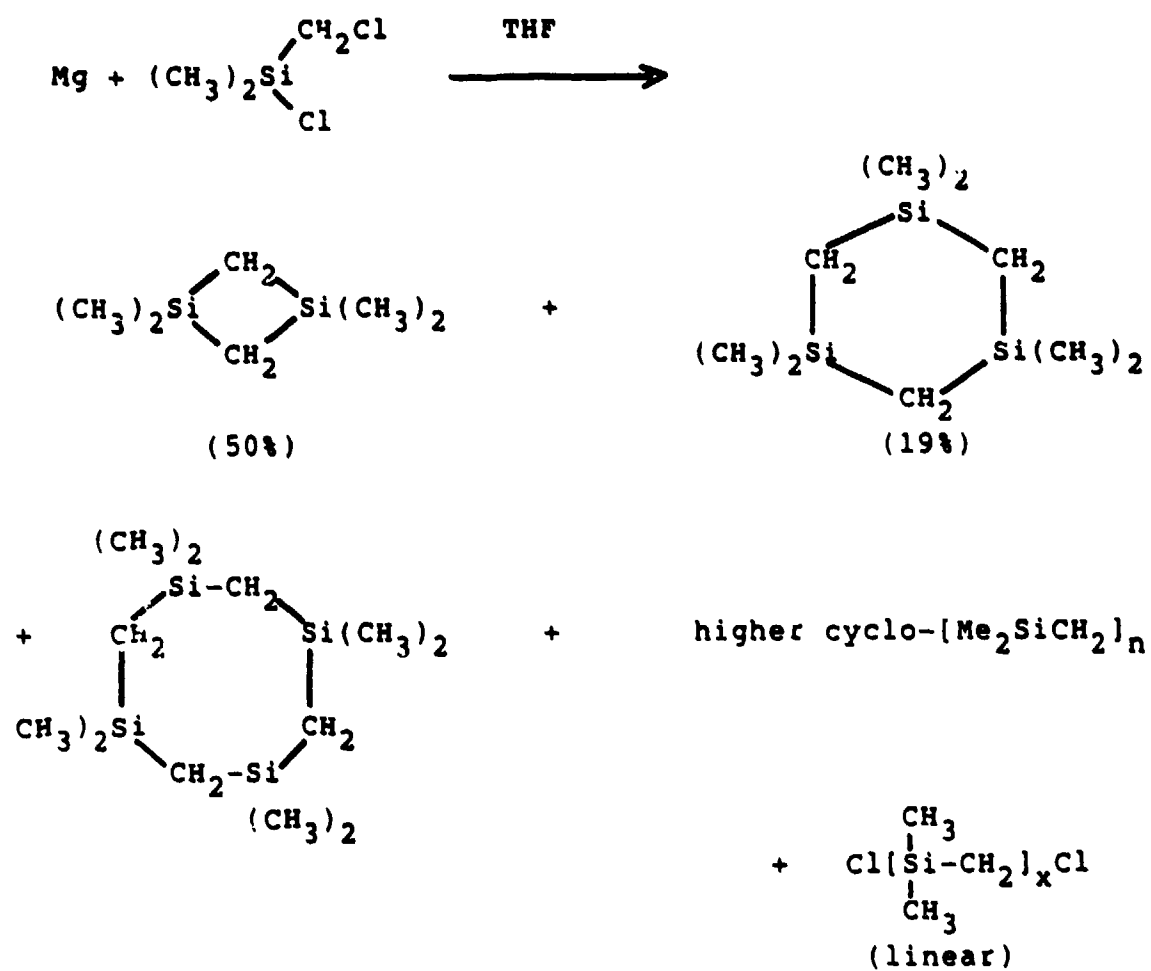
fraction, bp 150-250°C, left a residue of average molecular weight 850 (DP 11.8), with a viscosity of 300-400 cs at 25°C [8b].

In the sixties, such reactions were of greater interest as a source of 1,3-disilacyclobutanes (eq. 4) [9]. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane

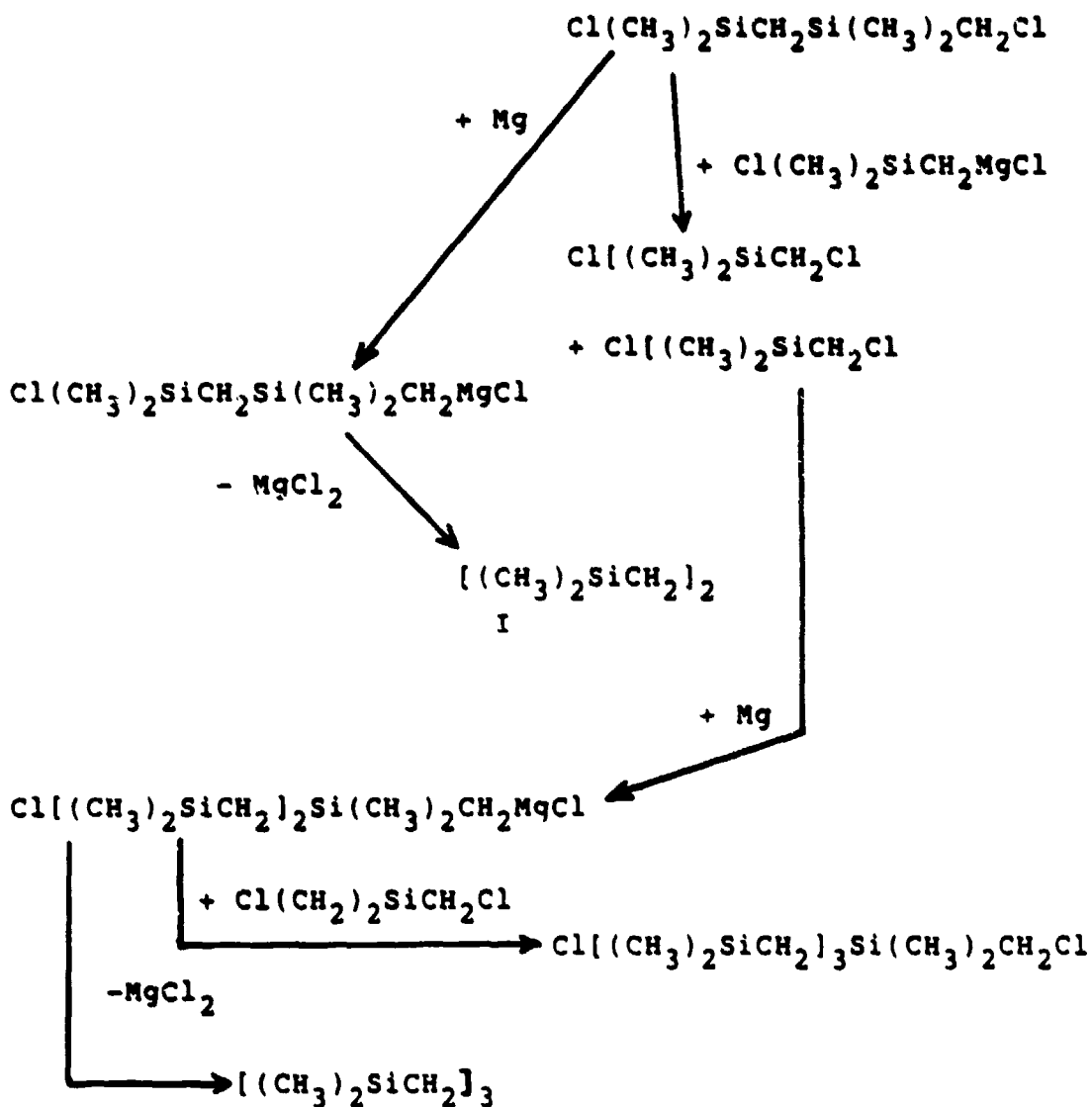
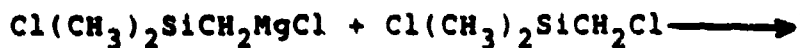
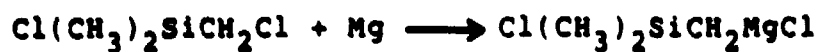


had been prepared earlier by Knoth and Lindsey [10], but a multistep synthesis was involved which was not generalizable to the synthesis of Si-functional 1,3-disilacyclobutanes. The reaction shown in eq. 4, provided it is carried out in the right way, represents a good, general route to 1,3-disilacyclobutanes. This reaction was reported first by Müller and his coworkers [11]. In this work, diethyl ether was used as reaction solvent and the product yield was only around 4%. Somewhat better yields were obtained by Russian workers [12], but it was the detailed studies of the (chloromethyl)chlorosilane/magnesium reaction by Kriner [13] which provided a good synthesis of 1,3-disilacyclobutanes. In most preparations of such compounds the yields generally are in the 30-60% range.

SCHEME 1



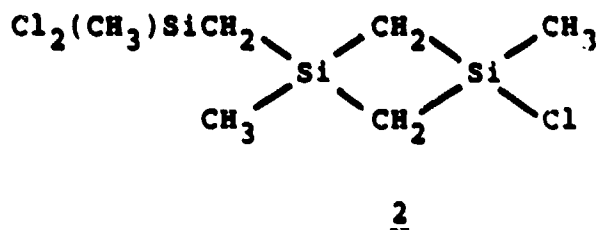
SCHEME 2



although in some cases they can be greater. Higher cyclic oligomers, cyclo- $[(CH_3)_2SiCH_2]_3$ and cyclo- $[(CH_3)_2SiCH_2]_4$ in the case of $(CH_3)_2(CH_2Cl)SiCl$, also are formed.

In spite of reaction conditions chosen to optimize formation of 1,3-disilacyclobutanes ("inverse addition", i.e., addition of the magnesium to a solution of the $RR'(CH_2Cl)SiCl$, high dilution), some linear, higher molecular weight product is formed (although this is not always mentioned in the description of the experiments by other authors). Scheme 1 depicts these various products and Scheme 2 shows the sequential organomagnesium coupling reactions believed to be responsible for their formation [13a]. Hydrolytic workup linked the linear species via siloxane bonds. Formation of linear polysilmethylene was the major process which occurred when $(CH_3)_2Si(CH_2Cl)Cl$ was added to a suspension of magnesium in diethyl ether or THF. In one such reaction carried out in THF, the yield of cyclo- $[(CH_3)_2SiCH_2]_2$ was only 6.7%, that of $[(CH_3)_2SiCH_2]_3$ 1.4%, and the main product was a viscous, opaque residue, molecular weight about 930 [13b].

When the starting (chloromethyl)chlorosilane contained more than one Si-Cl bond, lower yields of the 1,3-disilacyclobutane were obtained due to side reactions resulting from the availability of more Si-Cl functions (in the case of $CH_3Si(CH_2Cl)Cl_2$, **2** was produced in addition to cyclo- $[CH_3(Cl)SiCH_2]_2$) and

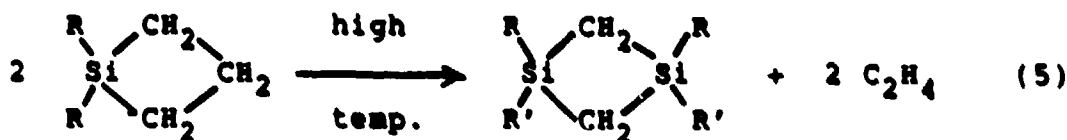


to formation of higher yields of polysilmethylene [13, 14].

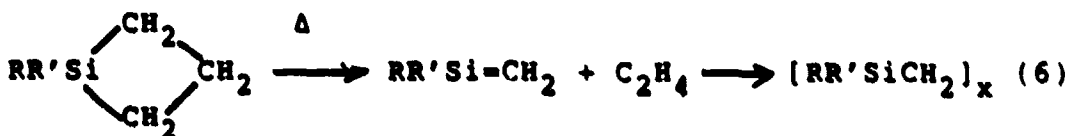
According to the available reports discussed above, the $RR'Si(CH_2Cl)Cl$ /metal reactions ($M = Na, Mg$) do not appear to give high molecular weight polysilmethylenes and at this time, this reaction has not found useful application in preceramic polymer synthesis. However, the introduction of crosslinking processes into the basic metal-effected dehalogenative polymerization of $(CH_3)_2Si(CH_2Cl)Cl$ was shown by Schilling and his coworkers [15] to result in formation of polycarbosilanes whose pyrolysis gave higher ceramic yields. Thus, cocondensation of $(CH_3)_2Si(CH_2Cl)Cl$ with

CH_3SiCl_3 by reaction with potassium in THF produced a branched polycarbosilane, $[(\text{CH}_3)_2\text{SiCH}_2]_x(\text{CH}_3\text{Si})_y$, which on pyrolysis to 1200°C gave a 31% yield of $\beta\text{-SiC}$. (This yield still is too low, and in further work, Schilling developed useful SiC polymer precursors which, however, are polysilanes, not polycarbosilanes [15].

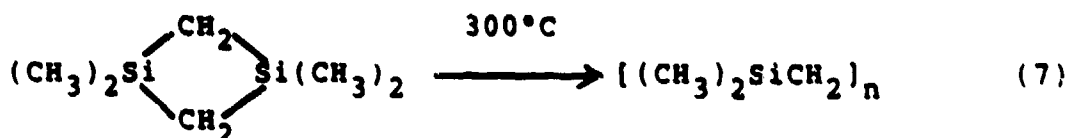
Another procedure for the synthesis of 1,3-disilacyclo-butanes is the pyrolysis of monosilacyclobutanes (eq.5), [9, 14, 16], but this method has difficulties and disadvantages [14]. One of these is that polysilmethylene formation is a side-reaction when it is carried out in the gas-phase.



Such polymerization apparently is the sole process when the silacyclobutane thermolysis is carried out in the liquid phase (eq. 6).



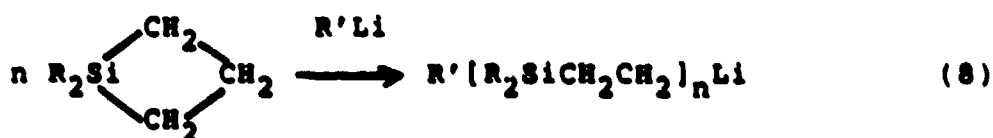
A more useful thermolytic polymerization which produces linear polysilmethylenes is that of 1,3-disilacyclobutanes carried out in the liquid phase. Such polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was reported first by Knoth [17] (eq.7). This process was studied in some detail by Russian workers [18]. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane is more



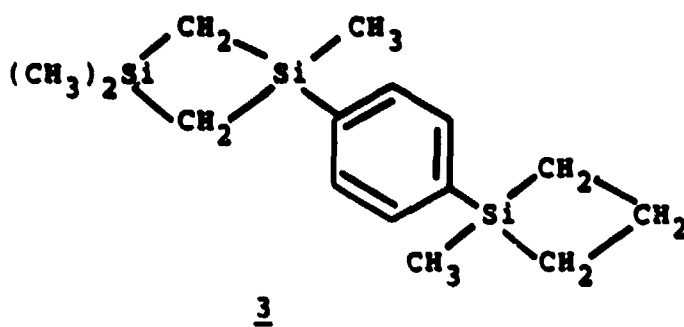
thermally stable than 1,1-dimethyl-1-silacyclobutane. Aryl and, more so, chlorine substituents on silicon enhance thermal stability of silacyclobutanes. The rate of the first-order thermal decomposition of silacyclobutanes varies inversely with the dielectric constant of the solvent used. Radical initiators have no effect on the thermal decomposition and a polar mechanism was suggested.

Thermal polymerization of cyclo- $[\text{Ph}_2\text{SiCH}_2]_2$ has been reported to occur at 180-200°C. The product was a crystalline white powder which was insoluble in benzene and other common organic solvents [19].

Anionic polymerization of 1,3-disilacyclobutanes also is possible. Solid KOH and alkali metal silanolates were mentioned as being effective by Russian authors [18, 19, 20]. However, alkyllithiums, which can initiate polymerization of silacyclobutanes (eq. 8) [21], do not initiate polymerization of 1,3-disilacyclobutanes [18,22]. The problem is one of steric hindrance.



The first intermediate, resulting from cyclo- $[(\text{CH}_3)_2\text{SiCH}_2]_2$ ring opening by RLi, is $\text{R}(\text{CH}_3)_2\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Li}$, a bulky "neopentyl"-type reagent. Its attack at another cyclo- $[(\text{CH}_3)_2\text{SiCH}_2]_2$ molecule will not be very favorable and so the polymerization does not progress. In fact, it is possible to polymerize 3 selectively via monosilacyclobutane ring opening using an organolithium initiator [18].



Transition metal catalysts are especially effective in initiating the ring-opening polymerization of 1,3-disilacyclobutanes to give polysilmethylenes, as reported by various workers [23-30]. Products ranging from low molecular weight telomers to high molecular weight polymers ($M_n \cdot 10^5$) could be prepared, depending on experimental conditions. A large variety of transition metal catalysts was applicable: Pt/C, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, PtCl_2 , IrCl_6^{2-} , RuCl_4^{2-} , AuCl_4^- , PdCl_2 , RuI_3 , $[\text{olefin PtCl}_2]_2$, $(\text{Et}_2\text{S})_2\text{PtCl}_2$, $(\text{Bu}_3\text{P})_2\text{Pt}_2\text{Cl}_4$, $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_3)_2$, $(\text{Pr}_3\text{As})_2\text{PtCl}_2$, PdBr_2 , AuCl_3 , CuCl_2 , CuCl , π -crotylnickel

and -chromium compounds, and others. The telomeric products of lower molecular weight were obtained when the catalytic 1,3-disilacyclobutane ring opening was carried out in the presence of small amounts of trialkylsilanes, R_3SiH [23, 24, 26], or carbon tetrabromide [26].

The high molecular weight $[(CH_3)_2SiCH_2]_n$ polymers are very thermally stable (2.0% weight loss after heating at 450°C in vacuo for 30 min [26]). However, pyrolysis under argon at 1000°C leaves little or no ceramic residue, so they are not useful preceramic polymers. Their thermal stability is poor in the presence of oxygen, polydimethylsiloxanes and formaldehyde and oxides of carbon being obtained as oxidation products. They are inert toward concentrated mineral acids and alkalis at room temperature, but chlorinolysis to lower molecular weight products occurs on photoinduced chlorination at 20°C [26]. Attempted conversion of $[(CH_3)_2SiCH_2]_n$ to $[CH_3(Cl)SiCH_2]_n$ by treatment with the $(CH_3)_3SiCl/AlCl_3$ silicon-methyl cleavage reagent did result in the desired methyl group cleavage, but the polymer of initial molecular weight 250,000 underwent chain scission, i.e., Si-CH₂ cleavage as well, to give $[CH_3(Cl)SiCH_2]_n$ products of average molecular weight 2300 [31].

Most of the polymerization studies were carried out with $[(CH_3)_2SiCH_2]_n$. The platinum-catalyzed polymerization of cyclo- $[CH_3(EtO)SiCH_2]_2$ and cyclo- $[CH_3(Cl)SiCH_2]_2$ gave only low yields of viscous liquid polymers [25]. Each of these monomers was copolymerized with cyclo- $[(CH_3)_2SiCH_2]_2$. Since the Si-H bond also is activated by transition metal catalysts, such catalyzed ring-opening polymerization of cyclo- $[CH_3(H)SiCH_2]_2$ very likely would present complications. Fairly low molecular weight $[CH_3(H)SiCH_2]_n$ oligomers were, however, accessible by another route: the $LiAlH_4$ reduction of the $[CH_3(Cl)SiCH_2]_n$ oligomers mentioned above [31]. In spite of their potentially useful reactive Si-H functionality, pyrolysis of these oligomers gave a ceramic yield of only 5%. Thus, a facile thermal crosslinking process did not occur.

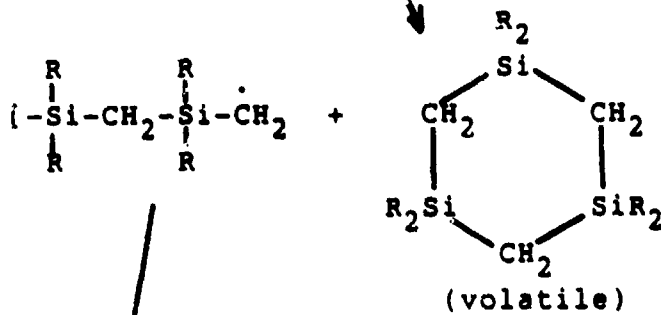
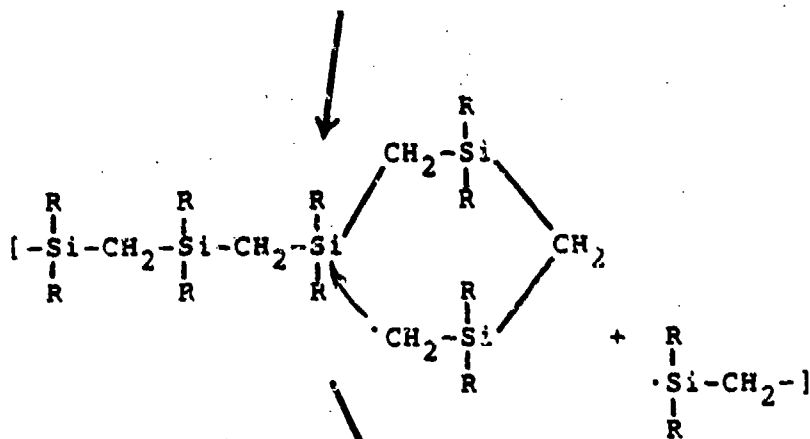
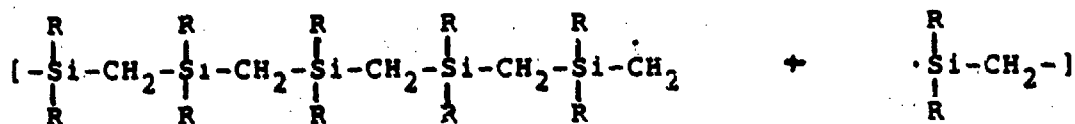
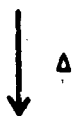
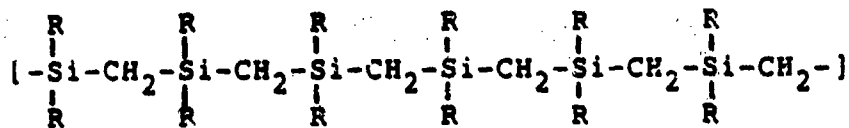
Polydimethylsilylene, $[(CH_3)_2SiCH_2]_n$, has received detailed study by Mark and his coworkers at the University of Cincinnati [32]. This polymer was prepared by $H_2PtCl_6 \cdot 6H_2O$ -catalyzed ring opening polymerization (at 25°C for 3 days) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The polymeric product was fractionated by precipitation from benzene by addition of methanol and the fractions obtained were characterized using viscosity, osmotic pressure and dielectric constant measurements. Samples of the polymer which had been

crosslinked by γ -radiation [32a] or a peroxide cure [32d] also were investigated (stress-strain isotherms and thermoelastic properties) in order to obtain useful information about the statistical properties of these chain molecules. The experimental and theoretical studies indicated that the most appropriate model for the $[(\text{CH}_3)_2\text{SiCH}_2]_n$ chain is one in which there is no strong preference for any conformation: most are of identical energy [32b]. Also studied was the stress-optical behavior of polydimethylsilylene [32c,d].

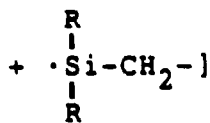
The polysilmethylenes, however, apparently are not useful polymers, either as such or as precursors for silicon carbide. A rubbery material could be prepared by treatment of $[(\text{CH}_3)_2\text{SiCH}_2]_n$ with dicumyl peroxide in the presence of fused silica and ground quartz, but no utility was claimed for this product [26]. The probable reason that polysilmethylenes are not useful preceramic polymers is that on pyrolysis they undergo chain scission. The reactive chain end thus generated, most likely a free radical center, then undergoes "back-biting", i.e., $\text{S}_{\text{H}}2$ attack further along the chain with resulting extrusion of a small, volatile, cyclic species (cyclo- $[(\text{CH}_3)_2\text{SiCH}_2]_n$ ($n = 2,3,4,\dots$)) in the case of polydimethylsilmethylene, as shown in Scheme 3. The result is that no residue is left behind as the polymer pyrolysis proceeds; all or most of the polymer is converted to volatiles. An apparent exception to this is the case of cyclo- $[\text{H}_2\text{SiCH}_2]_2$ which was reported to have been polymerized by catalytic activation with $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at 75°C in vacuo to give a "viscous liquid or a clear cake" which was claimed to "have a linear polycarbosilane structure" [33]. Pyrolysis of this material to 900°C , it was claimed, gave an 85% yield of silicon carbide. It seems doubtful that a linear polymer had been formed.

Polysilmethylene chains also are formed in the thermal, copper-catalyzed reactions of methylene chloride and chloroform with elemental silicon. Reported first by Patnode and Schiessler in 1945, the CH_2Cl_2 -Si/Cu reaction produced $\text{Cl}_3\text{SiCH}_2\text{SiCl}_3$, $\text{Cl}_3\text{SiCH}_2\text{SiCl}_2\text{H}$ and cyclo- $[\text{Cl}_2\text{SiCH}_2]_3$ as isolable products [34]. Also formed in this reaction was a viscous liquid product of approximate composition $[\text{Cl}_2\text{SiCH}_2]_n$. However, it was the work of Fritz and Wörsching [35] which led to the utilization of the CH_2Cl_2 -Si/Cu reaction in the formation of silmethylenes of higher molecular weight. The production of such species was optimized when the reaction was carried out in a fluidized bed reactor. For ease of analysis, all Si-Cl bonds in the product mixture were reduced to Si-H; this permitted the application of HPLC in the separation of

SCHEME 3



further S_H2
attack down
the chain



individual compounds in the product mixture. Those polysilmethylenes thus isolated and identified which contain four or more silicon atoms are shown in Table I. The CHCl_3 -Si/Cu reaction was carried out under the same conditions and also was followed by Si-Cl to Si-H reduction and HPLC. The branched polycarbosilane products thus isolated that contain four or more silicon atoms are depicted in Table II. These mixtures (or the higher molecular weight portions of these mixtures) present interesting possibilities as preceramic materials.

The polycarbosilanes which are precursors to the Nicalon ceramic fibers are not strictly polysilmethylenes. However, their main repeat units are $[\text{CH}_3(\text{H})\text{SiCH}_2]$ and $[(\text{CH}_3)_2\text{SiCH}_2]$, so they will be discussed here. The preparation of these polymeric precursors to silicon carbide as effected by S. Yajima and his coworkers was an important development [36]. The chemistry involved is fairly complex [36-39]. It is based on the thermal rearrangement of polydimethylsilylene (derived from sodium condensation of $(\text{CH}_3)_2\text{SiCl}_2$), initially, very likely to a polysilmethylene-type polymer as a result of a Kumada-type free radical rearrangement (which, in its simplest example converts, $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$ to $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{H}$ [40]). In the case of polydimethylsilylene, such a rearrangement would give as product $[\text{CH}_3(\text{H})\text{SiCH}_2]_n$. However, it is clear that the thermal conversion effected at 450-470°C does not stop there. IR and NMR spectroscopic studies have shown that the Yajima polycarbosilane has a more complicated structure than $[\text{CH}_3(\text{H})\text{SiCH}_2]_n$, and crosslinking and cyclization processes [such as that shown below (no mechanism implied)] have been suggested [41]. Ultimately, this would result in a polymeric product containing cyclic and polycyclic units linked by linear bridges. A structure which contains such building blocks, suggested by Yajima [36], is shown in Fig. 1. Such a structure, on pyrolysis, should leave a higher yield of ceramic residue than the linear $[\text{CH}_3(\text{H})\text{SiCH}_2]_n$. This is indeed the case. In one procedure, the yellowish-brown, glassy polycarbosilane which was obtained by heating the polydimethylsilylene at 450-470°C in an autoclave was heated at 280°C/1 mm Hg to remove volatiles. Pyrolysis of this material left a residue of silicon carbide and free carbon. The pyrolysis process has been investigated in some detail by Hasegawa and Okamura using spectroscopy, TGA-DTA and gas evolution studies [42]. The ceramic yields obtained on pyrolysis of such products usually are around 60%. These polycarbosilanes can be melt-spun

TABLE I

Compounds containing 4 or more Si atoms from the reaction of CH_2Cl_2 with Si, after hydrogenation

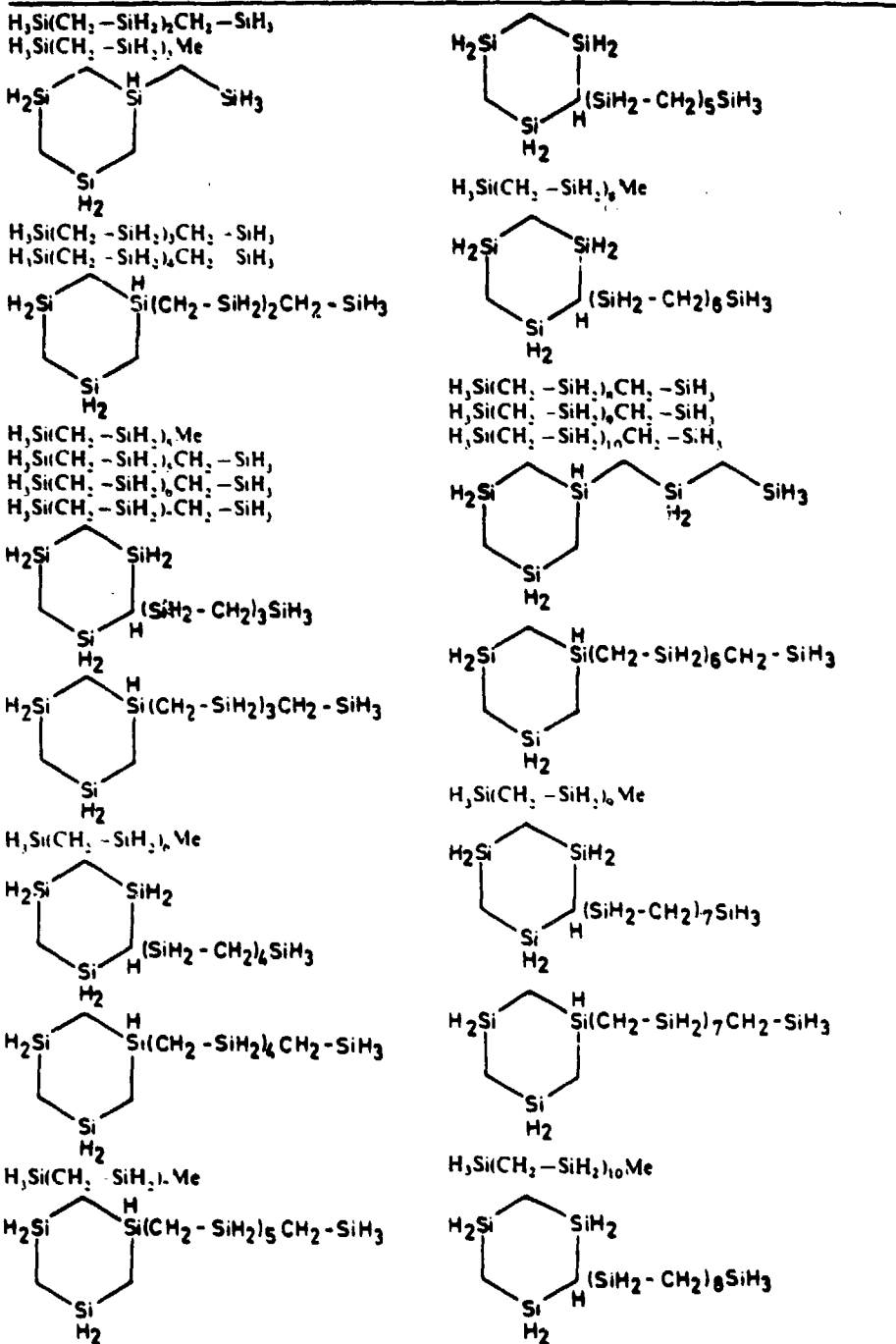
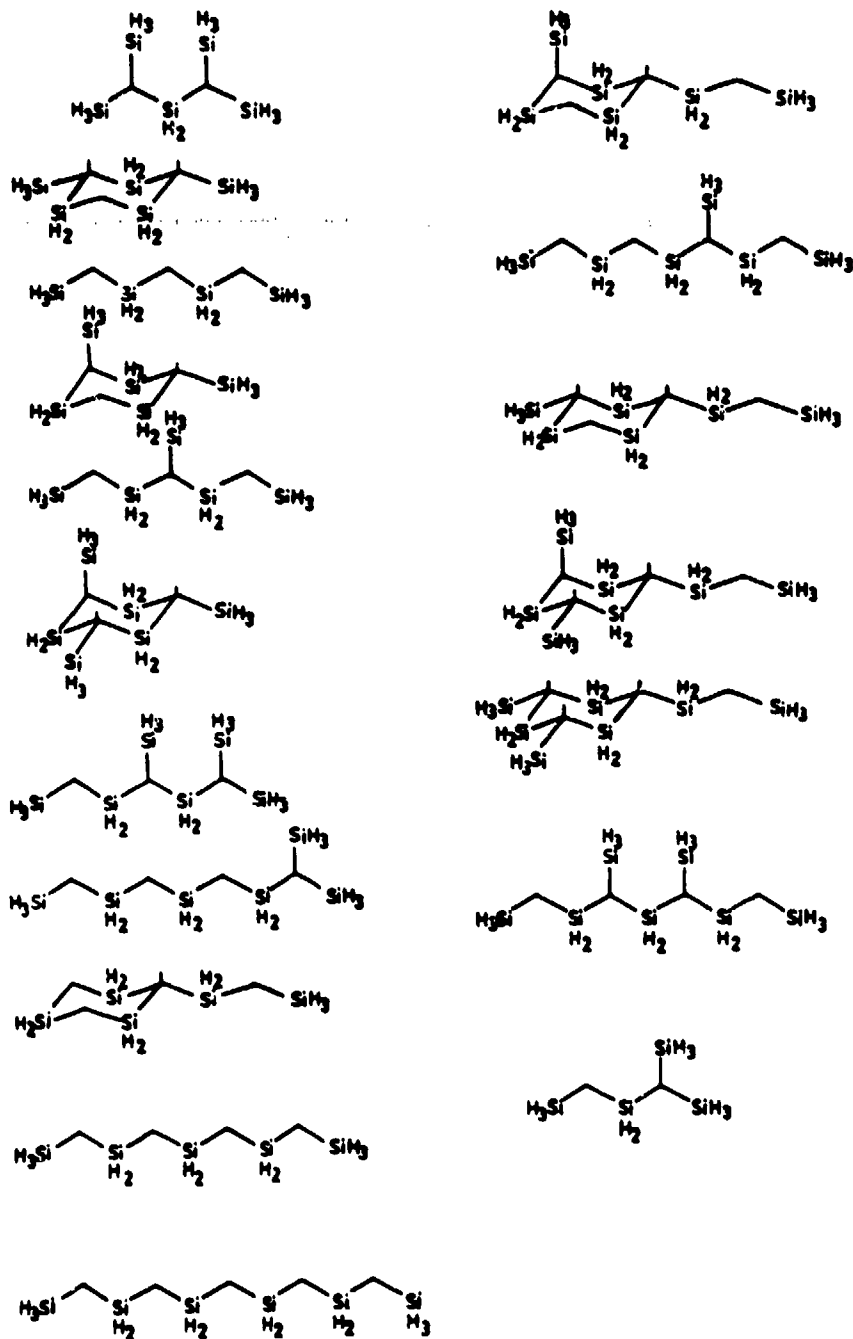
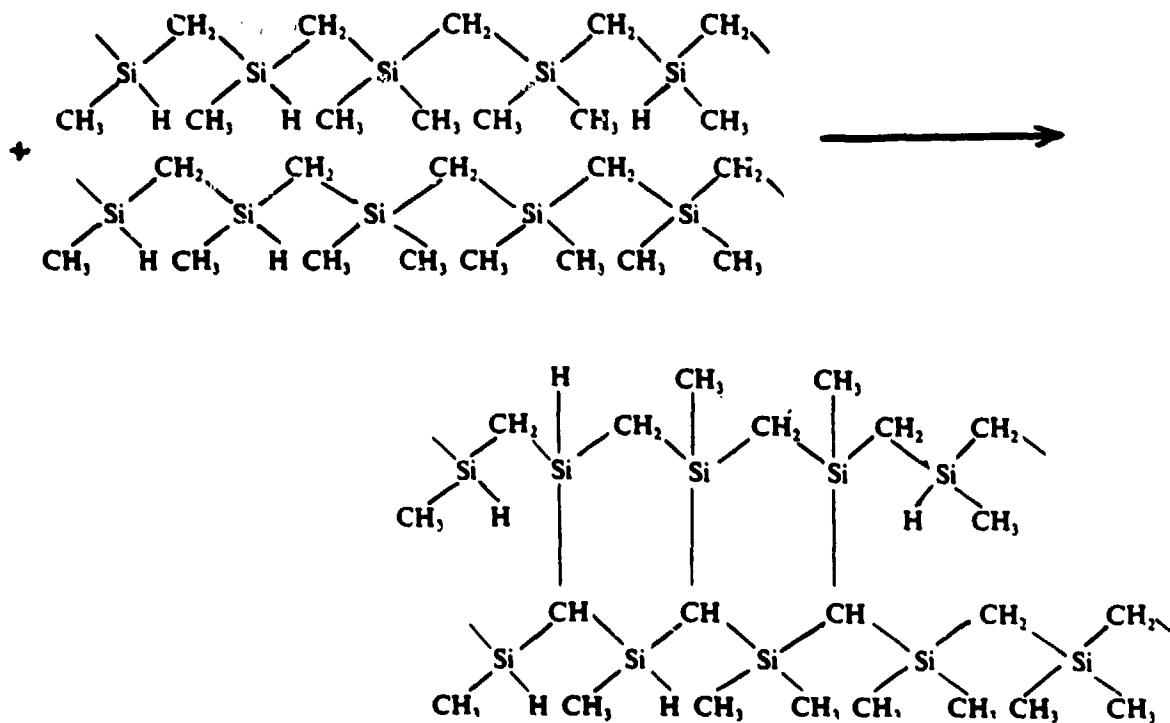


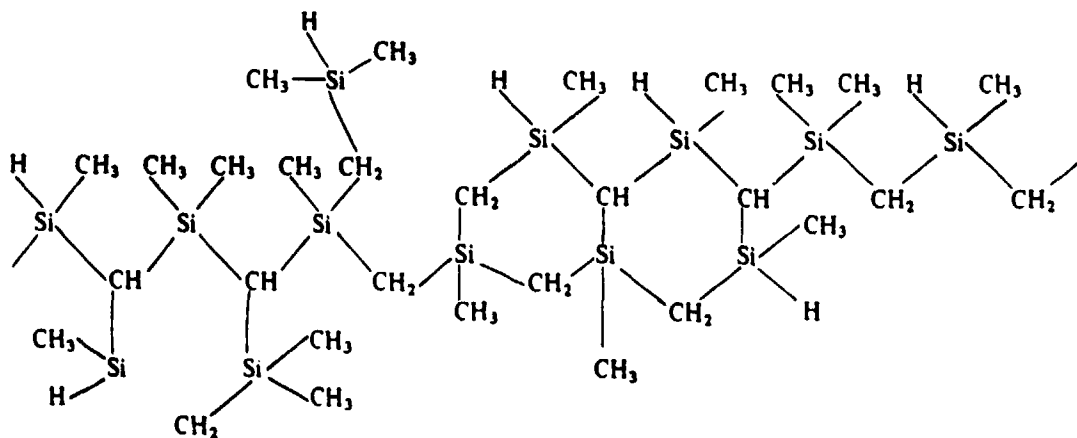
TABLE II

Compounds obtained from the reaction of Si with CHCl_3 after conversion of SiCl to SiH groups. Only compounds containing more than 4 Si atoms are shown





into continuous fibers and the latter, after an oxidative cure step to render them infusible, can be pyrolyzed to give black ceramic fibers, the so-called Nicalon fibers which are commercially available [43].



There are other variations of the basic Yajima polycarbosilane. In one case, the polydimethylsilylene is mixed with a few weight percent of a polyborodiphenylsiloxane prior to thermal rearrangement. This additive (which ends up in the polymeric product) serves to accelerate the rearrangement process so that it can be carried out at 350°C at atmospheric pressure [42]. In another variation, the polycarbosilane obtained from the polyborodiphenylsiloxane-induced thermal rearrangement ($M_n = 950$) was heated in xylene at 130°C to 220°C with $Ti(OC_4H_9)_4$ to produce a more highly crosslinked ($M_n = 1674$) Ti-containing polycarbosilane [44]. Crosslinking occurs via Si-O-Ti-O-Si linkages and pyrolysis of this polymer in a stream of nitrogen to 1700°C gave a ceramic product that contained (by X-ray diffraction) TiC as well as SiC. Pyrolysis to 1300°C gave a ceramic yield of around 72%. This type of Ti-containing polycarbosilane is a commercial product of Ube Industries.

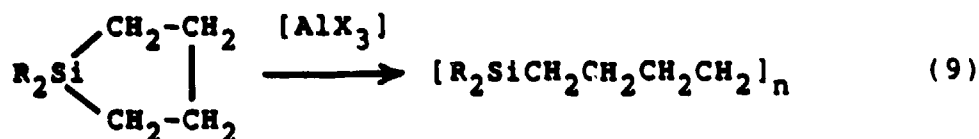
Another process for silicon carbide fibers, developed by Verbeek and Winter of Bayer AG [45], also is based on polymeric precursors which contain $[SiCH_2]$ units, although linear polysilmethylenes are not involved. The pyrolysis of tetramethylsilane at 700°C, with provision for recycling of unconverted $(CH_3)_4Si$ and lower boiling products, gave a polycarbosilane resin, yellow to red-brown in color, which was soluble in aromatic and in chlorinated hydrocarbons. Such resins could be melt-spun but required a cure-step to render them infusible before they were pyrolyzed to ceramic fibers. Oxidative and hydrolytic cures were mentioned. The pyrolysis of tetramethylsilane has been studied in great detail by G. Fritz and his coworkers and modern analytical, separation and spectroscopic techniques have enabled them to isolate and identify a large number of the products of this very complicated process [46] and to propose mechanisms for the thermolytic processes which result in their formation. (This work, which spans some 30 years, is summarized in ref. 1). During $(CH_3)_4Si$ pyrolysis, linear, cyclic and then polycyclic carbosilanes of ever increasing complexity are formed [46]. Some of the latter are shown in Tables III and IV. It will be appreciated that further condensation processes, occurring with further loss of the hydrogen and methyl substituents on carbon and silicon, will take place when products such as these are pyrolyzed. Their structures already give a hint of the final product, silicon carbide.

Yajima and his coworkers also studied tetramethylsilane thermolysis and used the resulting polycarbosilane in a fiber spinning investigation [42]. In

their experiments, in which the recirculating pyrolysis procedure of Fritz [47] was used, the yield of usable polycarbosilanes (bp > 200°C/1 mm Hg) of sufficiently high molecular weight ($M_n = 774$) was 6.8%. Its pyrolysis in a nitrogen stream to ca. 1300°C gave a ceramic yield of about 73%.*

In conclusion, the lesson learned from the research carried out to date on the subject of polycarbosilanes is that the general rule that linear, noncrosslinked polymers are not suitable preceramic polymers applies here as well. Crosslinked network-type polymers are needed. Such structures can be generated in more than one way, but in the case of the polycarbosilanes they have, to date, been obtained mainly by thermolytic routes: thermal treatment (with or without other chemical additives) in the case of the Yajima polycarbosilanes and the thermolysis of tetramethylsilane in the case of the Bayer process-derived polycarbosilane.

Although we have not discussed other types of polycarbosilanes, some may be mentioned to show what is available in terms of other specific examples of general formula 1. Already mentioned during the course of our discussion have been polymers of type $[R_2SiCH_2CH_2CH_2]_n$, obtained by ring-opening polymerization of monosilacyclobutanes. Such polymerization may be carried out thermally [48] or catalytically [20, 21, 24] (for reviews see ref. 9 and 18). Ring-opening polymerization of 1,1-disubstituted silacyclopentanes can be induced with an aluminum halide catalyst at temperatures ranging from 20°-80°C (eq. 9) [49]. (Silacyclohexanes did not polymerize under these conditions).



Also of interest are the thermal ring opening polymerizations of 1,1-dimethyl-1-silabenzocyclobutene (eq. 10) [50] and of 1,1,2,2-tetramethyl-1,2-disilabenzocyclobutene (eq. 11) [51]. The polymer produced in the latter reaction is a polycarbodisilane. These ring opening reactions proceed via Si-C

* Excessively high pyrolysis temperatures should be avoided: D. Seyferth and J.J. Pudvin, CHEMTECH 11 (1981) 230.

TABLE III Compounds produced by the pyrolysis of SiMe_4

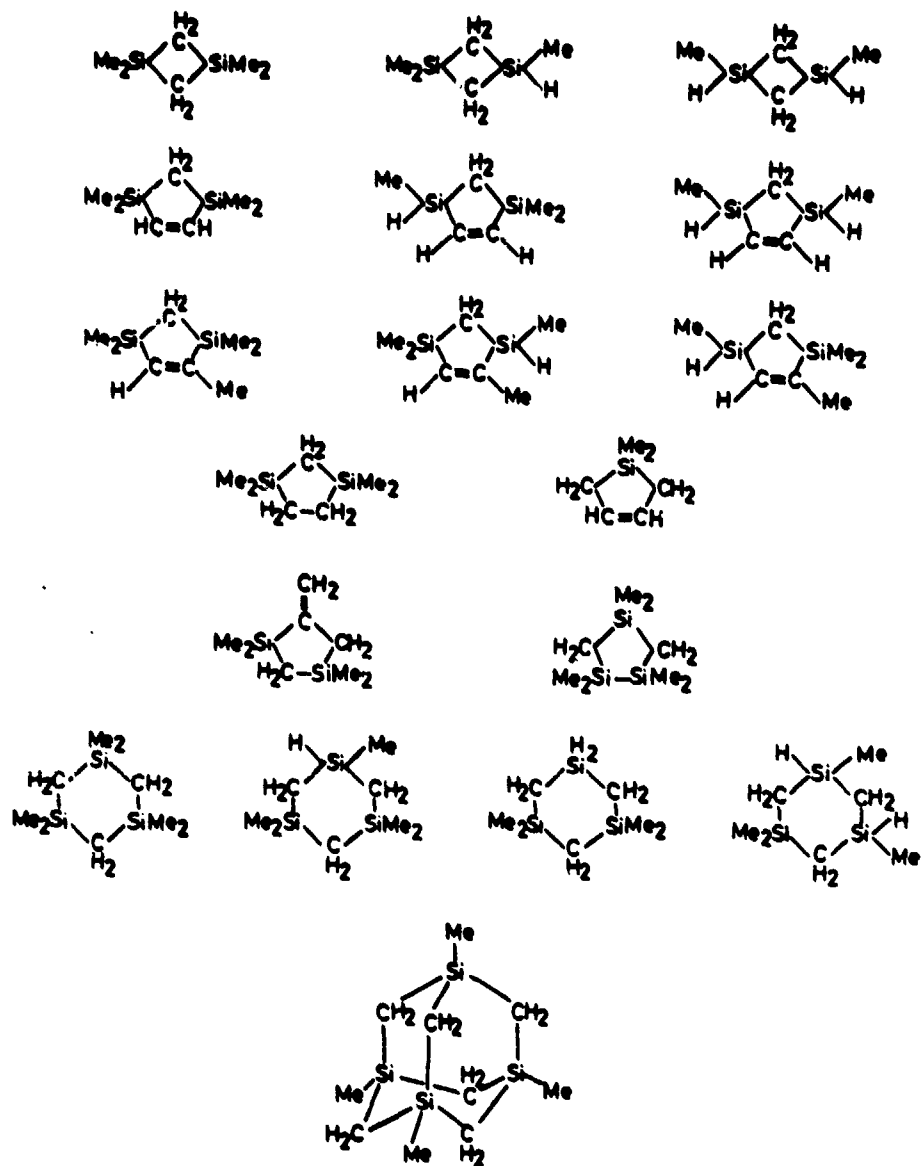


TABLE III

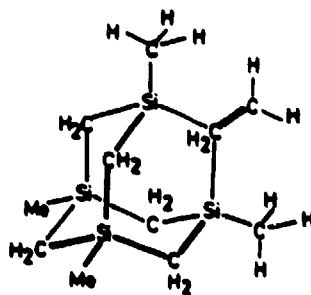
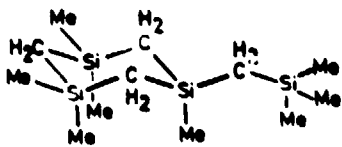
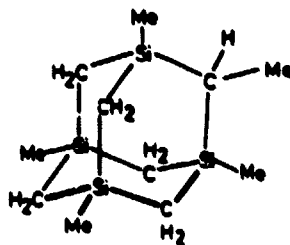
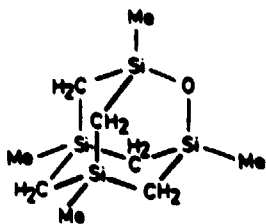
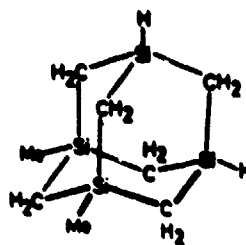
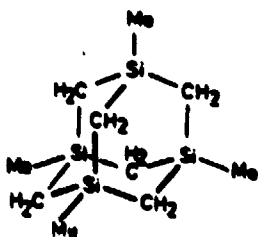
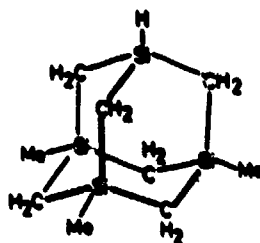
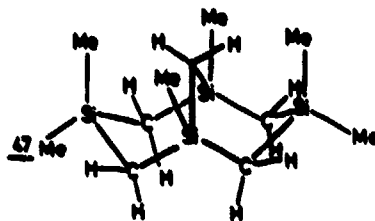
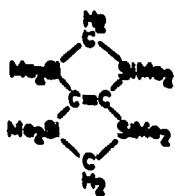


TABLE III

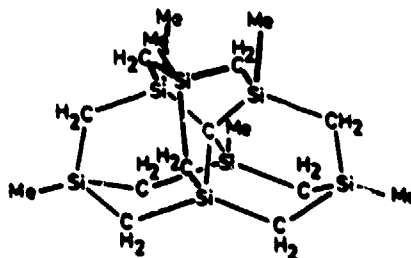
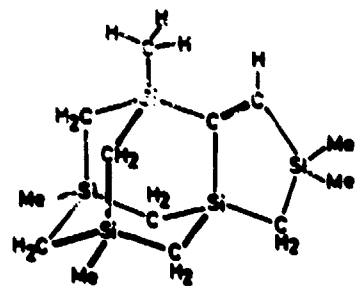
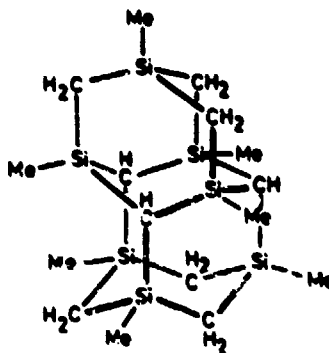
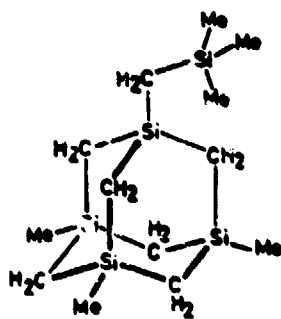
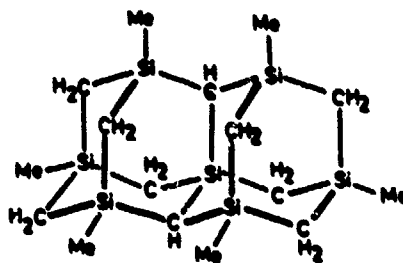
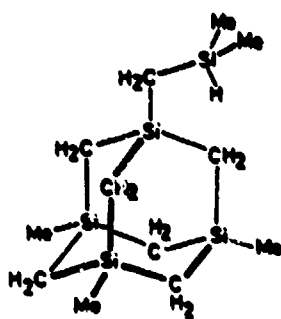
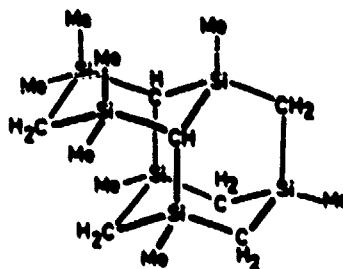
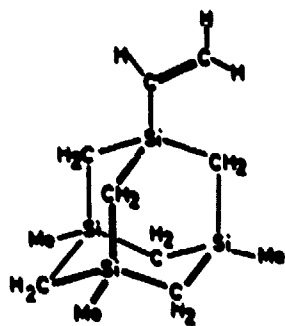
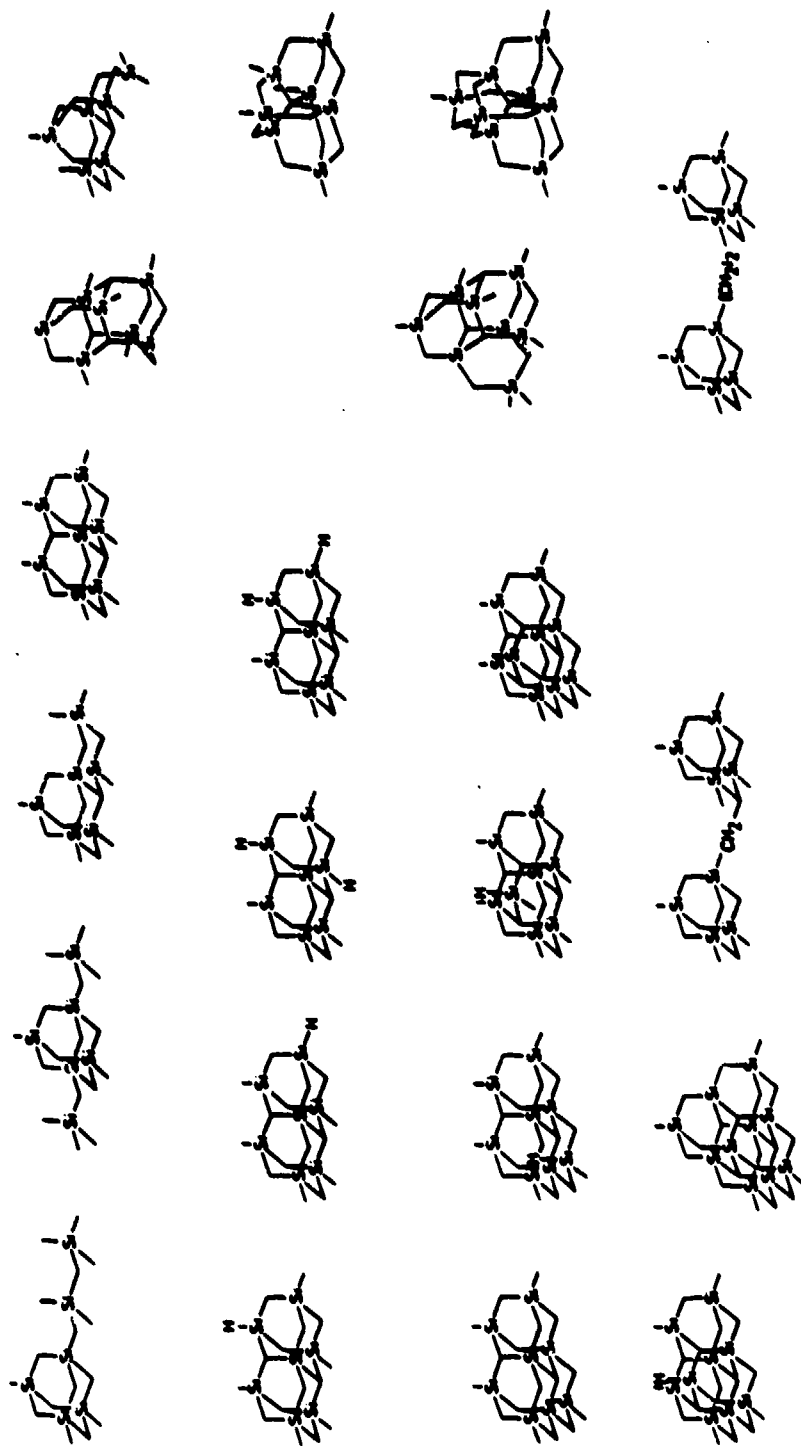
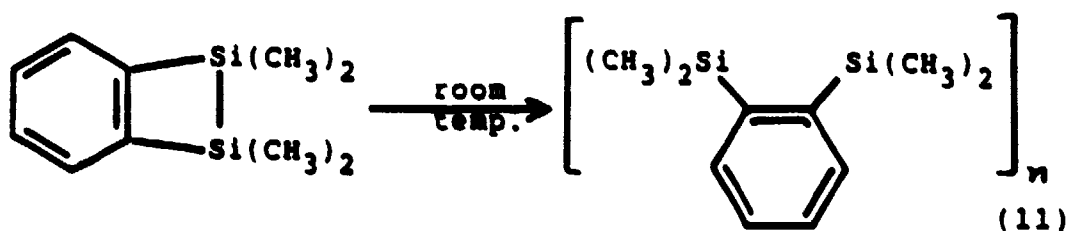
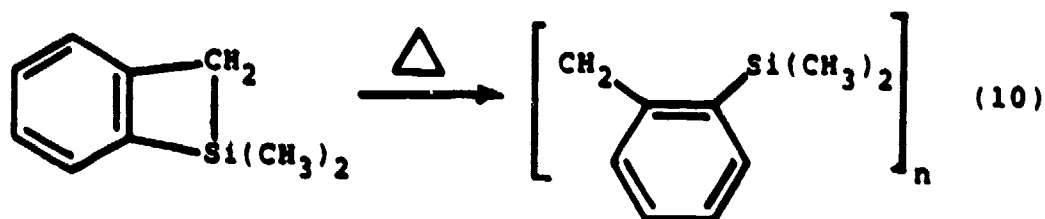


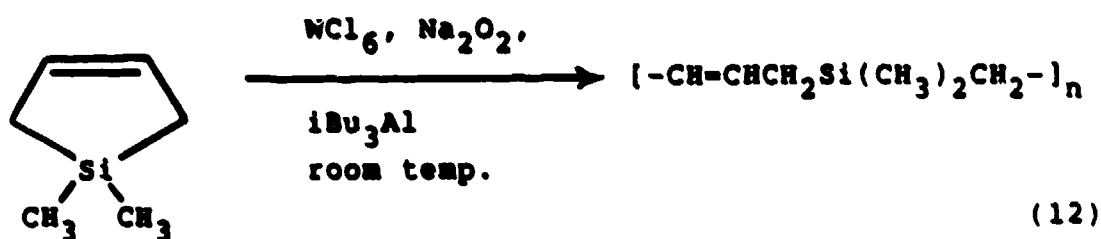
TABLE IV



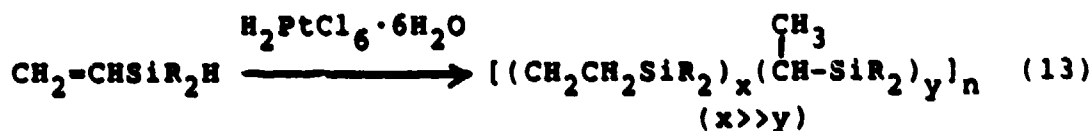
Carbodienes containing 5 to 8 silicon atoms, isolated by column chromatography and HPLC



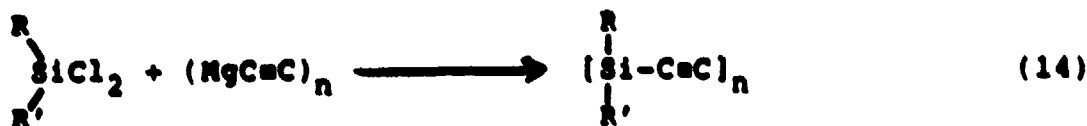
(or in the latter case, Si-Si) bond scission. Another type of ring-opening polymerization involves C=C bond scission (eq. 12) [52].



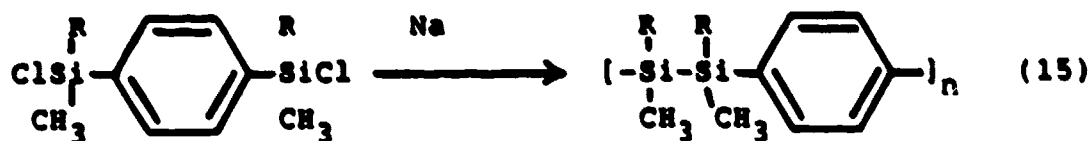
The hydrosilylation reaction has served in the polymerization of vinylsilicon hydrides (eq. 13) [53]. For the most part, β -addition predominated.



Polysilaacetylides have been prepared by the reaction so $\text{BrMgC}\equiv\text{CMgBr}$ [54], $(\text{MgC}\equiv\text{C})_n$ and $\text{LiC}\equiv\text{CLi}$ [55] with dichlorosilanes (eq. 14). In general, high molecular weight products were not obtained.



Silaarylene and silaarylene-siloxane polymers have been reviewed [56]. Recent work of interest on such systems is that of Koide and Lenz on poly(silaarylene-siloxanes) [57] and of Ishikawa et al. [58] on poly(p-(disilanylene)phenylenes), synthesized as shown in eq. 15.



(R = Et and Ph)

Ishikawa's polymers readily underwent photochemical degradation at specific frequencies, an observation which suggested their application as positive UV resists.

Acknowledgement

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REFERENCES

1. For a review of preceramic polymers, "Ceramics via Polymer Pyrolysis", see: K.J. Wynne and R.W. Rice, Ann. Rev. Mater. Sci., 14 (1984) 297-334.
2. G. Fritz and E. Matern, "Carbosilanes. Syntheses and Reactions", Springer-Verlag, Berlin, 1986.
3. E.G. Rochow, "An Introduction to the Chemistry of the Silicones", Wiley, New York; 1st edition, 1949, Chapter 3.
4. (a) L.H. Sommer, G.M. Goldberg, J. Gold and F.C. Whitmore, J. Am. Chem. Soc., 69 (1947) 980.
(b) B. Bluestein, J. Am. Chem. Soc., 70 (1948) 3068.
5. J.T. Goodwin, Jr., W.E. Baldwin and R.R. McGregor, J. Am. Chem. Soc., 69(1947) 2247.
6. (a) J.T. Goodwin, Jr., U.S. patent 2,507,512 (1950); Chem. Abstr., 45 (1951)3410.
(b) H.A. Clark, U.S. patent 2,507,517 (1950); Chem. Abstr.,45 (1951) 2259.
(c) H.A. Clark, U.S. patent 2,507,521 (1950); Chem. Abstr.,45 (1951) 2265.
(d) J.T. Goodwin, Jr., U.S. patent 2,544, 079 (1951); Chem. Abstr., 45 (1951)6654.
(e) J.T. Goodwin, Jr., Brit. patent 684,102 (1952).
7. L.H. Sommer, F.A. Mitch and G.M. Goldberg, J. Am. Chem. Soc., 71 (1949)2746.
8. (a) J.T. Goodwin, Jr., U.S. 2,483,972 (Oct. 4, 1949); Chem. Abstr., 44 (1950)2011e; Brit. 624,550 (June 10, 1949); Chem. Abstr., 44 (1950) 6632.
(b) J.T. Goodwin, Jr., U.S. 2,607,791 (1952); Chem. Abstr., 48 (1954) 13732.
9. For a review, which includes the synthesis, properties and reactions of 1,3-disilacyclobutanes see: R. Damrauer, Organometal. Chem. Rev., A, 8 (1972)67-133.
10. W.H. Knoth and R.V. Lindsey, Jr., J. Org. Chem., 23 (1958) 1392.
11. R. Müller, R. Köhne and H. Beyer, Chem. Ber., 95 (1962) 3030.
12. N.S. Nametkin, V.M. Vdovin, V.I. Zav'yalov and P.L. Grinberg, Izv. Akad. Nauk SSSR, Ser. Khim. (1965) 929.

13. (a) W. A. Kriner, J. Org. Chem., 29 (1964) 1601.
(b) W.A. Kriner, U.S. patent U.S. 3,178,392 (1965).
14. N. Auner and J. Grobe, J. Organomet. Chem., 188 (1980) 151.
15. (a) C.L. Schilling, Jr., J.P. Wesson and T.C. Williams, Amer. Ceram. Soc. Bull., 62 (1983) 912.
(b) C.L. Schilling, Jr., J.P. Wesson and T.C. Williams, J. Polymer Sci., PolymerSymposia, No. 70 (1983) 121.
(c) C.L. Schilling, Jr., Brit. Polymer J., 18 (1986) 355.
16. (a) N.S. Nametkin, V.M. Vdovin, L.E. Gusel'nikov and V.I. Zav'yalov, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1966) 584 [563].
(b) N.S. Nametkin, L.E. Gusel'nikov, V.M. Vdovin, P.L. Grinberg, V.I. Zav'yalov and V.D. Oppengeim, Dokl. Akad. Nauk S.S.S.R., 171 (1966) 630[1116].
(c) N.S. Nametkin, R.L. Ushakova, L.E. Gusel'nikov, E.D. Babich and V.M. Vdovin, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1970) 1676 [1589].
(d) L.E. Gusel'nikov and M.C. Flowers, Chem. Commun., (1967) 864.
(e) M.C. Flowers and L.E. Gusel'nikov, J. Chem. Soc. B. (1968) 419.
(f) C.M. Golino, R.D. Bush and L.H. Sommer, J. Am. Chem. Soc., 97 (1975) 7371.
(g) N.S. Nametkin, V.M. Vdovin and V.I. Zav'yalov, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1965) 1448.
(h) N. Auner and J. Grobe, J. Organomet. Chem., 197 (1980) 13.
(i) N. Auner and J. Grobe, J. Organomet. Chem., 197 (1980) 147.
(j) N. Auner and J. Grobe, Z. anorg. allg. Chem., 485 (1982) 53.
17. W.H. Knoth, U.S. 2,850,514 (1958); Chem. Abstr., 53 (1959) 4166a.
18. Review of ring opening reactions of silacyclobutanes: N.S. Nametkin and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 1153.
19. N.S. Nametkin, V.M. Vdovin and V.I. Zav'yalov, Dokl. Akad. Nauk SSSR, 162 (1965) 824.
20. N.S. Nametkin, V.M. Vdovin and V.I. Zav'yalov, Izv. Akad. Nauk SSSR, Ser. Khim. (1964) 203.
21. N.S. Nametkin, V.M. Vdovin, V.A. Poletaev and V.I. Zav'yalov, Dokl. Akad. Nauk. SSSR, 175 (1967) 1068.
22. D. Seyferth and J. Mercer, unpublished work, 1976.
23. N.S. Nametkin, V.M. Vdovin and P.L. Grinberg, Izv. Akad. Nauk SSSR, Ser. Khim. (1964) 1123.

24. D.R. Weyenberg and L.E. Nelson, J. Org. Chem. **30** (1965) 2618.
25. W. A. Kriner, J. Polymer Sci., Part A-1, **4** (1966) 444.
26. W.R. Bamford, J.C. Lovie and J.A. C. Watt, J. Chem. Soc. C (1966) 1137.
27. G. Levin and J.B. Carmichael, J. Polymer Sci., Part A-1, **6** (1968) 1.
28. N.S. Nametkin, N.V. Ushakov and V.M. Vdovin, Vysokomolekul. Soedin., **1** (1971) 29.
29. V.S. Poletaev, V.M. Vdovin and N.S. Nametkin, Dokl. Akad. Nauk SSSR, **203** (1972) 1324.
30. V.A. Poletaev, V.M. Vdovin and N.S. Nametkin, Dokl. Akad. Nauk SSSR, **208** (1973) 1112.
31. E. Bacqué, J.-P. Pillot, M. Birot and J. Dunoguès, Paper presented at the NATO Advanced Workshop on "The Design, Activation and Transformation of Organometallics into Common and Exotic Materials", Cap d'Agde, France, Sept. 1-5, 1986.
32. (a) J.H. Ko and J.E. Mark, Macromolecules, **8** (1975) 869.
(b) J.E. Mark and J.H. Ko, Macromolecules, **8** (1975) 874.
(c) M.A. Llorente, J.E. Mark and E. Saiz, J. Polymer Sci., Polymer Phys. Ed., **21**(1983) 1173.
(d) V. Galitsatos, and J.E. Mark, Polymer Preprints, **28** (1987) 258.
33. T.L. Smith, Jr., U.S. patent 4,631,179 (Dec. 23, 1986).
34. (a) W.I. Patnode and R.W. Schiessler, U.S. 2,381,000 and 2,381,002 (1945); Chem. Abstr. (1945) 4888.
(b) See also: A.V. Topchiev, N.S. Nametkin and V.I. Setkin, Chem. Techn., **4** (1952) 508; Dokl. Akad. Nauk SSSR, **82** (1952) 927.
35. G. Fritz and A. Wörsching, Z. anorg. allg. Chem., **512** (1984) 103.
36. (a) S. Yajima, Am. Ceram. Soc. Bull., **62** (1983) 893.
37. S. Yajima, M. Omori, J. Hayashi, K. Okamura, T. Matsuzawa and C. Liaw, Chem. Lett. (1978) 551.
38. For early Yajima papers see:
(b) S. Yajima, J. Hayashi and M. Omori, Chem. Lett. (1975) 931.
(c) S. Yajima, K. Okamura and J. Hayashi, Chem. Lett. (1975) 1209.
(d) S. Yajima, M. Omori, J. Hayashi, K. Okamura, T. Matsuzawa and C. Liaw, Chem. Lett. (1976) 551.
(e) S. Yajima, J. Hayashi, M. Omori and K. Okamura, Nature, **260** (1976) 683.

- (f) S. Yajima, K. Okamura, J. Hayashi and M. Omori, J. Am. Ceram. Soc., 59 (1976) 324.
39. S. Yajima, Y. Hasegawa, J. Hayashi and M. Iimura, J. Mater. Sci., 13 (1978) 2569.
40. (a) K. Shiina and M. Kumada, J. Org. Chem., 23 (1958) 139.
(b) H. Sakurai, R. Koh, A. Hosomi and M. Kumada, Bull. Chem. Soc. Japan, 39 (1966) 2050.
(c) H. Sakurai, A. Hosomi and M. Kumada, Chem. Commun. (1968) 930.
41. Y. Hasegawa and K. Okamura, J. Mater. Sci., 21 (1986) 321.
42. Y. Hasegawa and K. Okamura, J. Mater. Sci., 18 (1983) 3633.
43. Nippon Carbon Co. in Japan, via Dow Corning Corp. in the United States.
44. S. Yajima, T. Iwai, T. Yamamura, K. Okamura and Y. Hasegawa, J. Mater. Sci., 16 (1981) 1349.
45. W. Verbeek and G. Winter, Ger. Offenlegungsschrift 2,236,078 (1974).
46. G. Fritz and K.-P. Wörms, Z. anorg. allg. Chem., 512 (1984) 103.
47. G. Fritz, J. Grobe and D. Kummer, Advan. Inorg. Chem. Radiochem., 7 (1965) 349.
48. N.S. Nametkin, V.M. Vdovin and V.I. Zav'yalov, Izv. Akad. Nauk SSSR. Ser. Khim. (1965) 1448.
49. (a) V.M. Vdovin, K.S. Pushchevaya, N.A. Belikova, R. Sultanov, A.F. Plate and A.D. Petrov, Dokl. Akad. Nauk SSSR, 136 (1961) 96.
(b) N.S. Nametkin, V.M. Vdovin, K.S. Pushchevaya and V.I. Zav'yalov, Izv. Akad. Nauk SSSR, Ser. Khim. (1965) 1453.
50. (a) N.S. Nametkin, V.M. Vdovin, E. Sh. Finkel'shtein, M.S. Yatsenko and N.V. Ushakov, Vysokomolekul. Soedin. B11 (1969) 207.
(b) J.C. Salamone and W.L. Fitch, J. Polymer Sci., Part A 9 (1971) 1741.
51. K. Shiina, J. Organomet. Chem., 310 (1986) C57.
52. H. Lammens, G. Sartori, J. Siffert and N. Sprecher, J. Polymer Sci B. Polymer Lett., 9 (1971) 341.
53. (a) J.W. Curry, J. Am. Chem. Soc., 78 (1956) 1686.
(b) J.W. Curry, J. Org. Chem., 26 (1961) 1308.
54. L.K. Luneva, A.M. Sladkov and V.V. Korshak, Vysokomolekul. Soedin. A9, No.4 (1967) 910.
55. D. Seyferth, Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, San Diego, Feb. 23-27, 1987.
56. W.R. Dunnivant, Inorg. Macromol. Rev. 1 (1971) 165.

57. N. Koide and R.W. Lenz, J. Polymer Sci., Polymer Symposia, No. 70 (1983) 91.
58. (a) M. Ishikawa, N. Hongzhi, K. Matsusaki, K. Nate, T. Inoue, and H. Yokono, J. Polymer Sci., Polymer Lett. Ed., 22 (1984) 669.
- (b) M. Ishikawa, Polymer Preprints, 28 (1987) 426.

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