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Exploring novel silicon-containing polymers: from preceramic polymers to conducting polymers with nonlinear optical properties

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Pang, Yi, Ph.D.

Iowa State University, 1990

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Exploring novel silicon-containing polymers.
From preceramic polymers to
conducting polymers with nonlinear optical properties

by

Yi Pang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

Department: Chemistry
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For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1990

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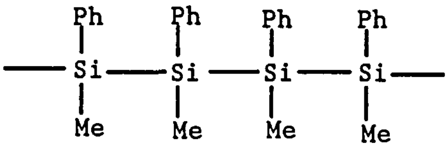
DEDICATION

TO JUAN

NOMENCLATURE

Polysilanes have backbones that consist entirely of Si-Si bonds. Currently two different systems are used to name polysilanes. Like simple organosilcon compounds, these polymers have been named using the -ane suffix. However there has been a trend to name this class of compounds in the same manner as the structural similar polyalkenes, using the -ene suffix. For example:

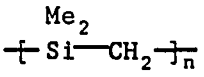


$$-\underset{\mathrm{Me}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\underset{\mathrm{Me}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\underset{\mathrm{Me}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\underset{\mathrm{Me}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-$$

poly(phenylmethylsilane)

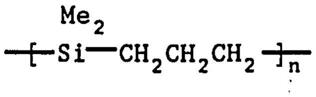
or poly(phenylmethylsilylene)

Polycarbosilanes have the Si-$(C)_x$-Si skeleton with $x \geq 1$. They are commonly named using the sil- prefix to denote the silicon atom in the chain, and the -ene suffix on the carbon group in the chain. Some examples are:



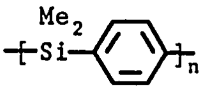
$$\left[\overset{\mathrm{Me_2}}{\mathrm{Si}}-CH_2\right]_n$$

poly(dimethylsilmethylene)

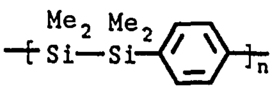


$$\left[\overset{\mathrm{Me_2}}{\mathrm{Si}}-CH_2CH_2CH_2\right]_n$$

poly(dimethylsilpropylene)

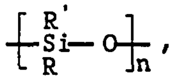


poly(dimethylsil-p-phenylene)



poly(tetramethyldisilanylene-p-phenylene)

INTRODUCTION

Silicon-containing polymers have been of great interests in both academia and industry because of their basic chemistry and unique properties which are not offered by other systems or materials. For example, polysiloxane (or silicone) which has a general formula  $\left[\begin{array}{c} R' \\ Si \\ R \end{array} - O \right]_n$, has developed and received wide applications ranging from electrical insulation to biomaterials and to space research. Some unique properties of polysiloxane include thermal and oxidative stability; little dependence of physical properties on temperature; resistance to weathering, ozone, and radiating; low surface tension; high surface activity; and chemical and biological inertness.

This thesis will be devoted to exploring several new silicon-containing polymer systems and their properties studies.

PART ONE. PRECERAMIC POLYMERS:
POLYSILACETYLENE AND POLYSILVINYLENE

INTRODUCTION

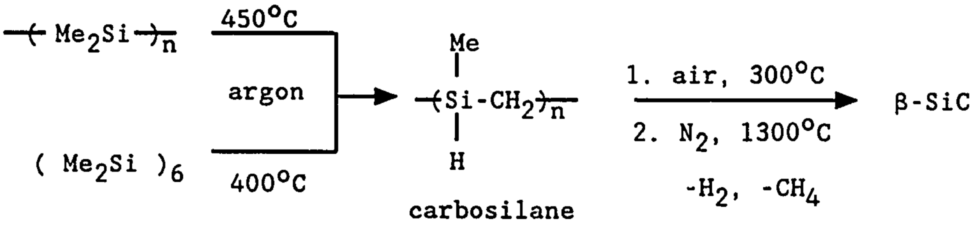
Silicon carbide[1], a well known hard material and an excellent thermal- and oxygen-resist ceramic, is a crystalline material with a color which varies from nearly clear through pale yellow or green to black depending upon the amount of impurities. Silicon carbide is commercially produced by the electrochemical reaction of high grade silica sand (quartz) and carbon (pitch coke) in an electric resistance furnace. The overall reaction is:

$$SiO_2 + 3C \xrightarrow{2600^\circ C} \alpha\text{-}SiC + 2CO$$

SiC prepared in this fashion is an intractable solid. This process takes 6-12 kWh energy to produce 1kg of crude SiC. Additional energy of about 1.5 kWh/kg is required to crush the crude SiC into usable grain. The metallurgical, abrasive, and refractory industries are the largest users of silicon carbide. It is also used for heating elements in electric furnaces, in electronic devices, and in applications where its resistance to nuclear radiation damage is advantageous.

Silicon carbide resists oxidation by forming a stable, oxygen-impermeable, silica surface coating[2]. Composition, especially the amount of carbon, plays a significant role in the oxidative stability of the ceramic alloy. The examination of the oxidative stability of a series of Si-C-N ceramic chars[3], which were produced by pyrolysis of silsesquiazanes $[RSi(NH)_{3/2}]_x$ at 1200°C, showed that the ceramics with more than 35-40 wt % free carbon oxidized completely to silica after 12 hours at 1200°C in air, whereas those with less than 25 % carbon content oxidized to only about 2 %. This result indicts that a large excess of carbon should be avoided in the ceramic product. Oxygen content in the ceramics has an important effect on the mechanical properties too. This can be shown in terms of Young's moduli for SiC, Si_3N_4, and SiO_2 of 410, 300, and 70 GPa($60x10^6$, $44x10^6$, and 10^6 psi) respectively. Clearly increasing the oxygen content (two bond per atom) will decrease the concentration of covalent bonds per unit volume, and so decrease the modulus.

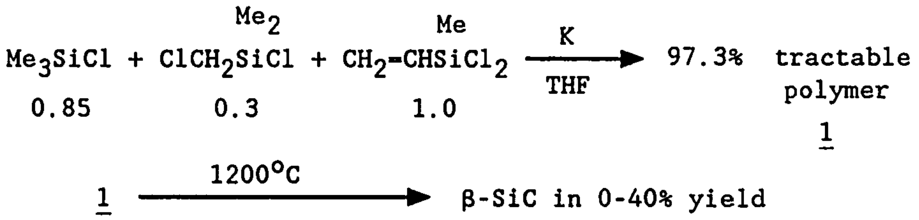
The superior mechanical properties and the extremely high softening temperature (mp=2700°C) of SiC have, however, presented a challenge for the fabrication of complex ceramic shapes like films and fibers. The use of preceramic polymers, which can be processed as ordinary polymers to the desired shape and then pyrolyzed to ceramics, can overcome this high temperature-shaping problem. This principle was first demonstrated by Yajima[4] in a two-step thermal conversion of polydimethylsilanes to SiC fiber. In the first step, the low-temperature pyrolysis converts the intractable poly(dimethylsilane) into a soluble carbosilane. The carbosilane thus produced is fractionated by solvent precipitation. The purified polycarbosilane produced with a 50-60 wt% yield is yellowish-brown glassy solid with an average Mw of 1000-2000. The soluble polycarbosilane can be melt spun into fibers. These fibers are then surface oxidized at temperatures between 350-400°C to provide dimensional stability for further processing, and then fired to 1300°C in an inert atmosphere to ultimately produce β-silicon carbide.



The Yajima process has been commercialized with SiC fiber and cloth being offered under the Nicalon trade name.

The additional steps necessary to produce first carbosilanes and then to oxidize to provide dimensional stability can be circumvented by the use of processible polysilane derivatives other than poly(dimethylsilane). West[5] reported that poly(methylphenylsilane) and poly(methylphenylsilane-co-dimethylsilane) ("polysilastyrene") could be melt extruded into fibers and fired to yield silicon carbide. In this process a photochemical cross-linking step is employed to provide dimensional stability prior to the high-temperature conversion. In mechanistic studies[6] on the conversion of linear polysilastyrene to silicon carbide it was reported that an initial polymer decomposition to lower molecular silicon hydrides is followed by recombination at high temperature.

Schilling et al.[7] reported a series of polycarbosilane precursors for silicon carbide. Reaction of a mixture of $ClCH_2Si(CH_3)_2Cl$, $CH_2{=}CH\text{-}Si(CH_3)Cl_2$ and $(CH_3)_2SiCl_2$ with potassium metal in THF gives a branched, soluble polycarbosilanes, which can be converted by known procedures at high temperature to SiC.

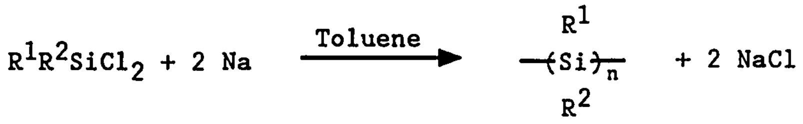


$$\underset{0.85}{Me_3SiCl} + \underset{0.3}{ClCH_2\overset{Me_2}{Si}Cl} + \underset{1.0}{CH_2{=}CH\overset{Me}{Si}Cl_2} \xrightarrow[THF]{K} 97.3\%\ \text{tractable polymer}\ \underline{1}$$

$$\underline{1} \xrightarrow{1200^{\circ}C} \beta\text{-SiC in 0-40\% yield}$$

In summary all the preceramic polymers to SiC developed so far are based on polysilanes. Although continuous progress has been made in this field, several intrinsic drawbacks existing in polysilane systems still seriously affect their processabilities, and finally limit their application in ceramics. First, homopolymers with identical nonflexible substituents, such as poly(dimethylsilane) or poly(diphenylsilane), are insoluble and infusible[8]. Introduction of flexible group like n-hexyl, or formation of copolymer has improved the solubility, however the poor solubility of high molecular weight polysilanes in common organic solvents still remains a problem.

Secondly, polysilanes are synthesized via a Wurtz-type coupling of dichlorosilanes[9]. The sodium is normally employed as a dispersion in an inert aromatic solvent such as toluene or xylene. In addition to the hazards associated with the use of large amounts of sodium metal, the polymer yields in this reaction are low, typically between 10-60%. This results in a big loss of the valuable silicon compounds during the polymerization. Another significant drawback in the Wurtz coupling reaction is the strong reducing ability of the metal and the vigorous reaction conditions (refluxing toluene) used.



$$R^1R^2SiCl_2 + 2\ Na \xrightarrow{\text{Toluene}} -\!\!\left(\overset{R^1}{\underset{R^2}{Si}}\right)_{\!n} + 2\ NaCl$$

Finally low ceramic yields are obtained[10] with polysilane precursors. This is shown in Table 1. The

Table 1. Polysilane polymers and their SiC yields[10]

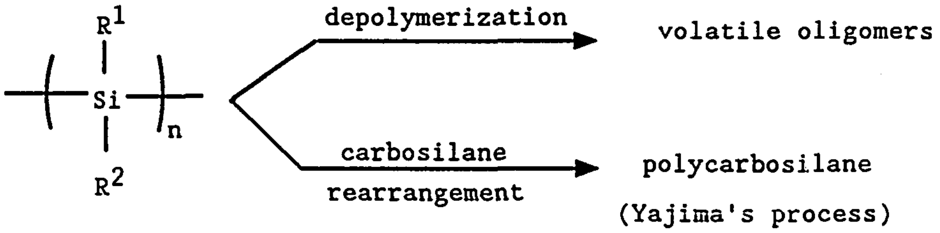
Polymer	Polymer yield (wt%)	Theoretical SiC yield (wt%)	Char yield (wt%)	SiC yield[a] (percent of theoretical)
(a) Homopolymers				
$(Me\text{-}Si\text{-}Me)_n$	75	69	1.0	1.2
$(C_6H_5\text{-}Si\text{-}Me)_n$	30	33	24.6	41.5
$(C_6H_{13}\text{-}Si\text{-}CH_3)_n$	60	31	5.8	17.5
(b) Copolymers				
$(C_6H_5\text{-}Si\text{-}CH_3)_{1.0}$ $(CH_3\text{-}Si\text{-}CH_3)_{1.0}$	14	51	13	15.4
$(CH_2{=}CH\text{-}Si\text{-}CH_3)_{1.0}$ $(C_6H_5\text{-}Si\text{-}CH_3)_{9.0}$	64	36	39.1	54.5
$(C_6H_5\text{-}Si\text{-}CH_3)_{1.0}$ $(C_6H_{13}\text{-}Si\text{-}CH_3)_{1.0}$	37	32	8	17.9

[a] SiC yields are calculated from elemental analysis results of the chars and their corresponding theoretical SiC yields.

loss of silicon component during the pyrolysis process makes the processing of SiC fiber difficult. Multi-step pyrolysis has to be used in Yajima's process in order to avoid large losses of the silicon component. An essential step in Yajima's process is to crosslink the polycarbosilane fibers in order to retain the shape of the fibers in the following high-temperature pyrolysis.

However the oxygen will be introduced and the mechanical properties of the SiC fibers will be decreased[11]. Polymer precursors for SiC with better processability are clearly needed.

The considerable weight loss during the pyrolysis of polysilanes most probably results from the weakness of the Si-Si bond. A significant depolymerization happens during the pyrolysis and competes with the carbosilane rearrangement. Introduction of some carbon into the polysilane backbone might improve the situation because the Si-C bond (89.4 kcal/mole for Si-CH_3)[12] is stronger than the Si-Si bond (74 kcal/mole for H_3Si-SiH_3).

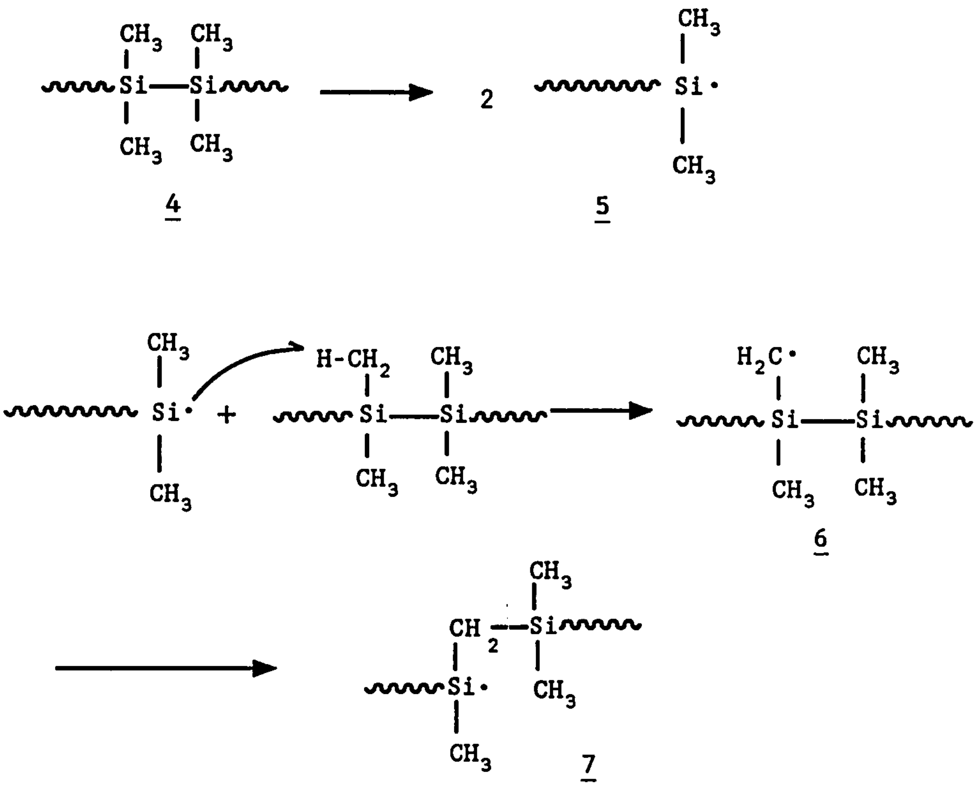


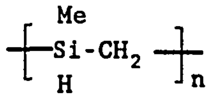
2

3

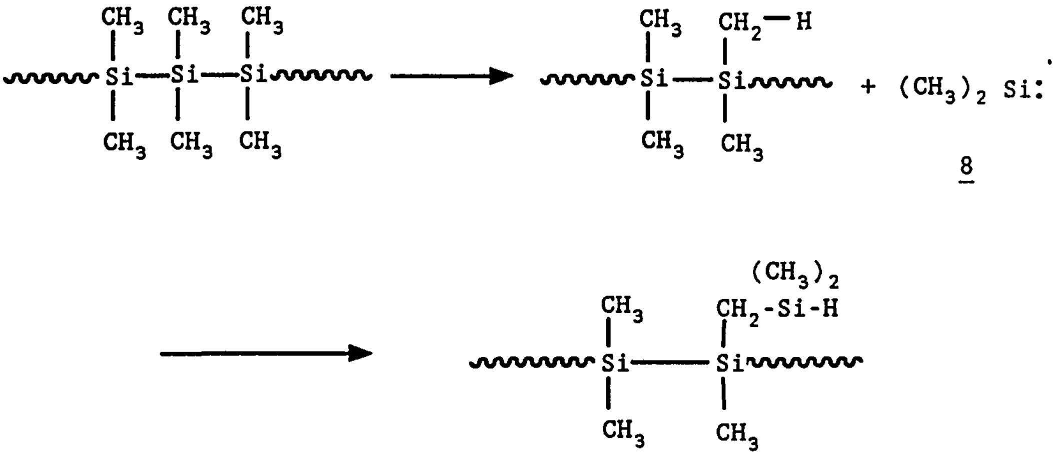
(1)

The mechanism for the carbosilane rearrangement in equation (1) has not been well understood. Potential intermediates are silyl radicals, carbon radicals, and silylenes which are generated by thermal 1,1-elimination. It was originally assumed that the rearrangement proceeds in a mechanism first suggested by Shuna and Kumada[13]. Silyl radicals 5 are generated under a thermal condition.



Extraction of proton of 5 from methyl in another molecule or segment produces a α-carbon radical 6 which then undergoes 1,2-silyl shift to give a carbosilane 7. Repeating this mechanism would lead to an ideal, linear polycarbosilane  $\left[\underset{\mathrm{H}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\text{-}\mathrm{CH_2} \right]_n$.

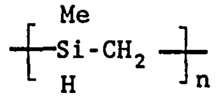
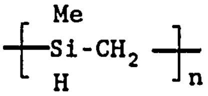
An mechanistic alternative would be 1,1-elimination followed by C-H insertion of the silylene. The structure of the polycarbosilane thus obtained is probably more complex than the linear structure 7 shown above since a branched or even crosslinked structure can be expected here. The silylene 8 is generated under a thermal

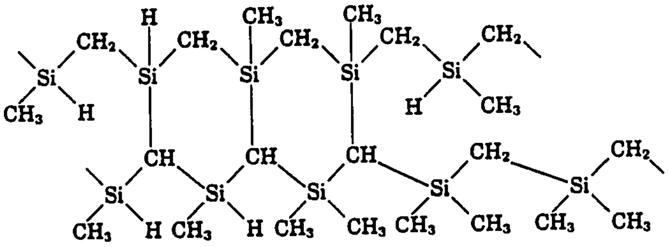


8

9

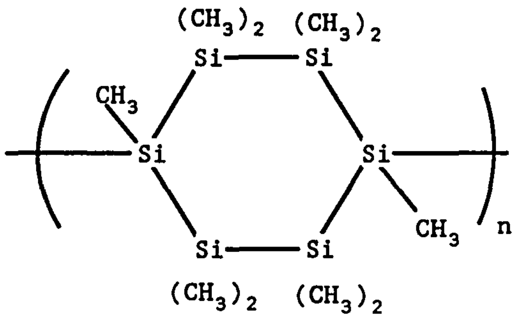
condition via 1,1-elimination. Insertion of 8 into the C-H bond gives carbosilane 9. No evidence, however, has been observed to support the "silylene insertion" mechanism.

The chemical structure of the polycarbosilane 3 is more complicate than the linear structure  $\left[\overset{Me}{\underset{H}{Si}}-CH_2 \right]_n$. Bacque et al.[14] reported that the linear polycarbosilane  $\left[\overset{Me}{\underset{H}{Si}}-CH_2 \right]_n$ with Mn 2000-2200 (PDI 1.9) was oil-like which is contrasted with the high-melting temperature of polycarbosilane from Yajima's process (mp 220~300°C, Mn=1750). Poor char yield (5%) of the linear polycarbosilane further suggests that polycarbosilane 3 does not possess a linear structure. Based on the NMR studies (^1H, ^{13}C and ^{29}Si), Hasegawa and Okamura[15] have suggested that the polycarbosilane obtained in the Yajima's process has a planar structure 10 containing both linear and ring



10

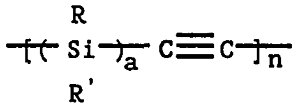
segments. There are about 3-4 linkages between chains in the polymer unit of 10 silicon atoms. So it is probably the ring segment in the chain that increases the thermal stability of the polycarbosilane. Because of the ring segment in the polymer backbone, the depolymerization process is suppressed. This can be explained by the lower probability to cleave two parallel bonds (required to cleave off a ring structure from polymer chain) than to cleave an independent bond in the depolymerization of a linear polymer. Kumar and Litt[16] recently reported that poly(permethylcyclohexasilane) 11 has a char yield of 51% (theoretical yield 75%) which is much higher than the one for linear poly(dimethylsilane) (char yield 1.0%;



11

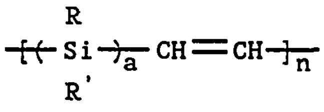
theoretical yield 69%)[10].

Introduction of some unsaturated functionalities in the polysilanes, either in the polysilane backbones or side groups, might increase the char yields for the pyrolysis process. The silyl radical or other reactive intermediates generated during the pyrolysis will be trapped by the existing unsaturated groups. So formation of some ring segments or crosslinking might occur before the depolymerization proceeds. Thus depolymerization will be suppressed and the loss of silicon components will be decreased or avoided during the pyrolysis. The polymers like 12 and 13 have not been well studied,



$$\left[\left(\underset{R'}{\overset{R}{\mathrm{Si}}}\right)_a \mathrm{C}\equiv\mathrm{C}\right]_n$$

12



$$\left[\left(\underset{R'}{\overset{R}{\mathrm{Si}}}\right)_a \mathrm{CH}=\mathrm{CH}\right]_n$$

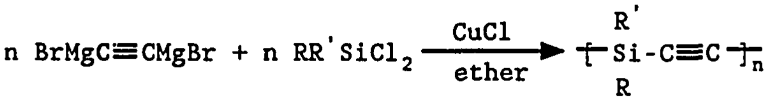
13

especially their thermal properties. This section of the thesis will be devoted to the synthetic studies of these type of polymers and the examination of their thermal properties which play a key role in their transformation to SiC material.

LITERATURE SURVEY

Poly(diorganosilacetylene) 12

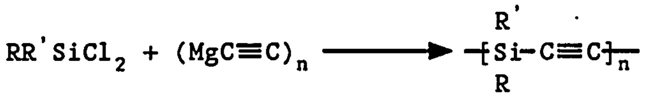
The syntheses of silicon-acetylene compounds are generally accomplished by one of two methods[17]: (1) the reaction of alkali acetylides with organosilicon halides, and (2) the corresponding reaction of acetylenic Grignard compounds with organosilicon halides. Several polymers of poly(diorganosilacetylene) type 12 were first synthesized by Korshak et al.[18] through the condensation of acetylene dimagnesium bromide with dichlorosilanes. The color of the obtained polymer ranged from yellow to dark brown.



$$n\ \mathrm{BrMgC{\equiv}CMgBr} + n\ \mathrm{RR'SiCl_2} \xrightarrow[\text{ether}]{\text{CuCl}} \left[\overset{R'}{\underset{R}{\mathrm{Si}}} - \mathrm{C{\equiv}C} \right]_n$$

R	R'	Mw	solubility
CH_3	CH_3	--	not soluble
CH_3	Ph	2700	soluble in benzene
Ph	Ph	1400	soluble in benzene

Seyferth et al.[19] reported the condensation of magnesium acetylide with dichlorosilanes to generate low molecular weight silylene-acetylene. The magnesium acetylide was prepared from the reaction of commercial dibutylmagnesium with gaseous acetylene.

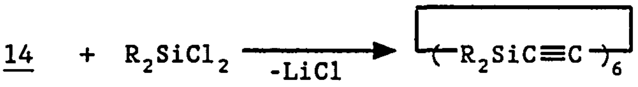


$$RR'SiCl_2 + (MgC{\equiv}C)_n \longrightarrow -\!\!\left[\overset{R'}{\underset{R}{Si}}-C{\equiv}C\right]_n\!\!-$$

R	R'	Mw
CH_3	CH_3	insoluble
CH_3	H	900
CH_3	$CH_2{=}CH$	1100

Bortolin et al.[20] found that reaction of dilithium derivatives of diorganodiethynylsilanes 14 with the corresponding diorganodichlorosilanes afforded the cyclic compounds 15 or 16 in ≥90% yield.

$$R_2Si(C{\equiv}CH)_2 + 2\ n\text{-}BuLi \xrightarrow[-BuH]{} \underset{\underline{14}}{R_2Si(C{\equiv}CLi)_2}$$



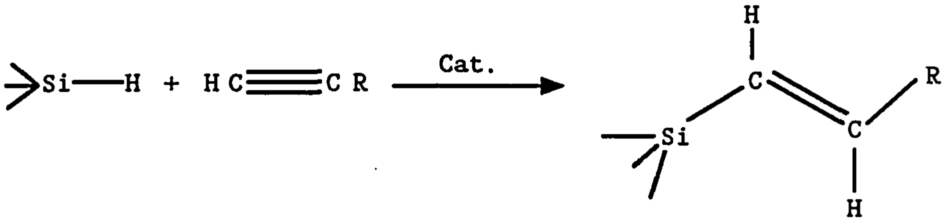
$$\underline{14} + R_2SiCl_2 \xrightarrow[-LiCl]{} \left(R_2SiC{\equiv}C\right)_6$$

15; R = Me

16; R = Ph

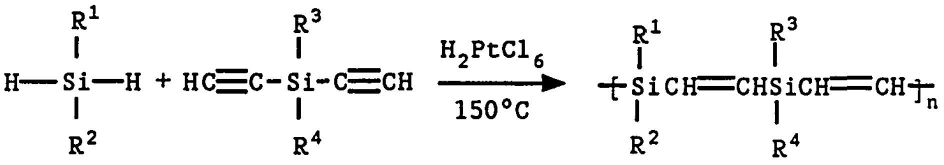
Poly(diorganosilvinylene) 13

Silicon-vinyl compounds can be conveniently formed via hydrosilation, that is, addition of Si-H bond across an acetylene in the presence of a catalyst[21]. Most often the catalyst is a platinum based complex, although rhodium, ruthenium complexes and sometimes radical



initiators can be used.

Korshak et al.[22] reported that reaction of

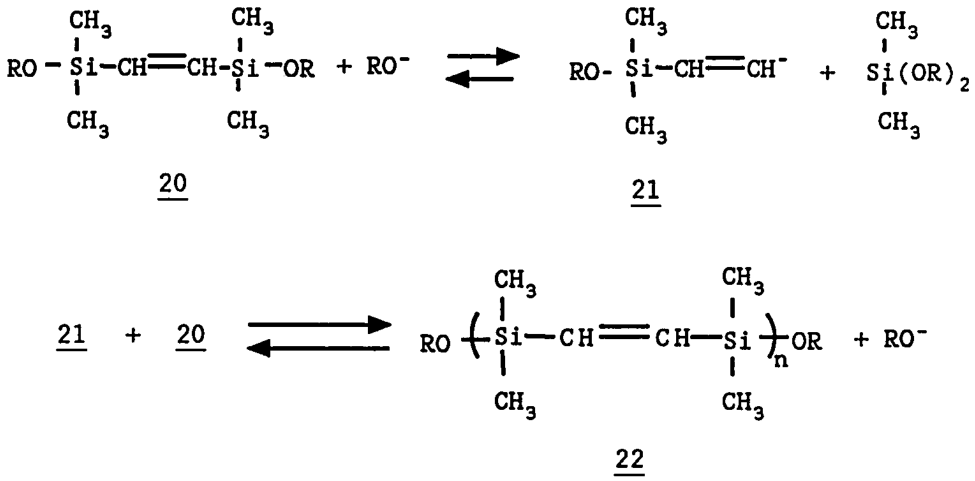


17 18 19

R^1	R^2	R^3	R^4	Mw
CH$_3$	Ph	CH$_3$	Ph	--
CH$_3$	Ph	Ph	Ph	6000

diorganosilane 17 with diorganodiethynylsilane 18 in presence of a catalytic amount of chloroplatinic acid at 150°C for 5 hours afforded brown product 19. No spectroscopic data except IR were reported.

Andrianov et al.[23] reported another synthetic route which started with bis(dimethylethoxysilyl)ethylene 20. The disproportionation of compound 20 in the presence of a catalytic amount of potassium hydroxide at 190°C produced soluble brown polymer 22. No molecular weight was reported in the paper. From the ESR measurement, the spin count for polymer <u>22</u> was determined to be 1x10^{16} spin/gram (possibly from an impurity in the polymer). Except elemental analysis, no other characterizations were reported.



$$RO-Si(CH_3)_2-CH{=}CH-Si(CH_3)_2-OR + RO^- \rightleftharpoons RO-Si(CH_3)_2-CH{=}CH^- + (CH_3)_2Si(OR)_2$$

20 21

$$\mathbf{21} + \mathbf{20} \rightleftharpoons RO\left(Si(CH_3)_2-CH{=}CH-Si(CH_3)_2\right)_n OR + RO^-$$

22

RESULTS AND DISCUSSION

Poly(diorganosilacetylene)

The synthesis of poly(silylene-acetylene) could be achieved by the condensation of dimetal acetylides with dichlorosilanes[17-20]. To our knowledge, however, high molecular weight poly(diorganosilacetylene) had not been reported. The goal of this research was to develop new methods to synthesize these polymers with high molecular weights.

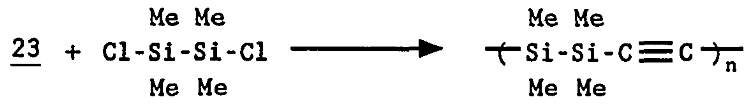
The condensation of acetylene dimagnesium chloride with dichlorosilanes was performed without CuCl to see if CuCl played any role in the polymerization. White solids were obtained with similar molecular weights as reported by Korshak et al.[18(a)]. Likewise,

$$HC\equiv CH + 2CH_3MgCl \xrightarrow{THF} \underset{\underline{23}}{ClMg\text{-}C\equiv C\text{-}MgCl} + CH_4\uparrow$$

$$\underline{23} + R_2SiCl_2 \longrightarrow \left(\overset{R_2}{Si}-C\equiv C\right)_n$$

$\underline{24}$ R = CH_3, Mw = 3000,

$\underline{25}$ R = Ph, Mw = 4000,



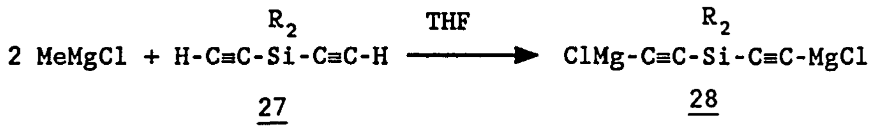
$$\underline{23} + Cl\text{-}\underset{Me}{\overset{Me}{Si}}\text{-}\underset{Me}{\overset{Me}{Si}}\text{-}Cl \longrightarrow \left(\underset{Me}{\overset{Me}{Si}}\text{-}\underset{Me}{\overset{Me}{Si}}\text{-}C\equiv C\right)_n$$

$\underline{26}$ Mw = 4000

poly(tetramethyldisilanyleneacetylene) 26 was for the first time synthesized by substituting $ClMe_2SiSiMe_2Cl$ for R_2SiCl_2. Both higher reaction temperatures and longer reaction times failed to generate higher Mw products.

The relative low Mw of the product obtained in the diGrignard, $ClMgC{\equiv}CMgCl$, route might originate from either or both of the following two reasons: (1) the difficulty in making pure diGrignard, and (2) incomplete reaction between 23 and the dichlorosilanes used. In our hands, synthesis of 23 was found a tedious work. Because of the difficulty in recognizing the point at which the bubbling of acetylene should be stopped, the diGrignard acetylide 23 prepared this way may always contain some ethynylmagnesium chloride which will act as a terminating agent in the polymerization.

The use of diethynylsilane 27 as a starting material has several advantages over the diGrignard $ClMgC{\equiv}CMgCl$ route. First in diGrignard 28 two negative charges are well separated which makes preparation of the diGrignard easier. Purer diGrignard would therefore be expected under the same conditions. Secondly, half of the $MgCl_2$ salts are removed by simply choosing 27 as a starting material. This will reduce the difficulty in stirring which is encountered during the reaction. Although this route is easier to perform, not much improvement was



$$2\ \mathrm{MeMgCl} + \underset{\underline{27}}{\mathrm{H{-}C{\equiv}C{-}}\overset{R_2}{\mathrm{Si}}\mathrm{{-}C{\equiv}C{-}H}} \xrightarrow{\mathrm{THF}} \underset{\underline{28}}{\mathrm{ClMg{-}C{\equiv}C{-}}\overset{R_2}{\mathrm{Si}}\mathrm{{-}C{\equiv}C{-}MgCl}}$$

$$\underline{28} + R_2SiCl_2 \longrightarrow \begin{array}{l} \underline{24}\quad R = Me,\ Mw = 4000 \\ \underline{25}\quad R = Ph,\ Mw = 5000 \end{array}$$

observed with molecular weights.

Voronkov et al.[24] reported the dehydrocondensation of trialkylsilanes with several acetylenes in good yields in presence of catalytic amount of H_2PtCl_6 and I_2.

$$Et_3Si{-}H + H{-}C{\equiv}CR \xrightarrow{H_2PtCl_6/I_2} Et_3SiC{\equiv}CR + H_2\uparrow$$

89% when R=Ph

96% when R=Bu

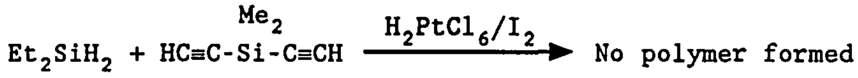
The author proposed the following mechanism for the dehydrocondensation via silyl iodide as intermediate.

$$R_3SiH + I_2 \longrightarrow R_3SiI + HI$$

$$R_3SiI + HC{\equiv}CR' \rightleftarrows R_3SiC{\equiv}CR' + HI$$

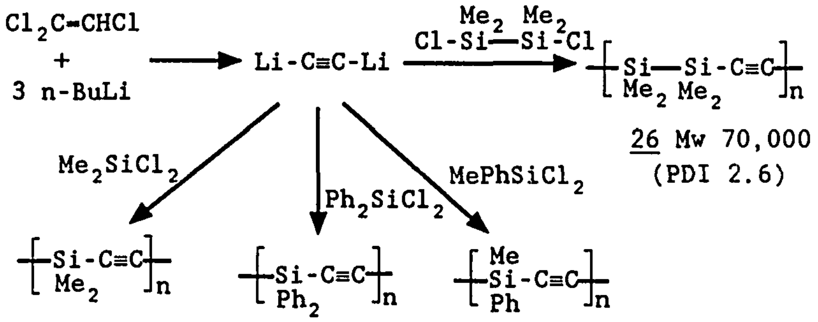
$$R_3SiH + HI \longrightarrow R_3SiI + H_2\uparrow$$

Utilization of the same catalyst in the reaction between diethylsilane and dimethyldiethynylsilane, however, failed to generate any polymer product. After the reaction mixture was stirred for overnight, there was no any dehydrocondensation product found by GC-MS except starting materials.



$$Et_2SiH_2 + HC{\equiv}C\text{-}\overset{Me_2}{Si}\text{-}C{\equiv}CH \xrightarrow{H_2PtCl_6/I_2} \text{No polymer formed}$$

In our continuous efforts to improve the Mw for these polymers, Dr. Ijadi-Maghsoodi[25] discovered that dilithium acetylide could be quantitatively generated via a reaction of trichloroethylene (TCE) with three equivalents of n-BuLi. This dilithium acetylide could be directly used to couple with a variety of dichlorosilanes. Very high Mw was obtained with this route.



26 Mw 70,000
(PDI 2.6)

24 Mw 20,000
(PDI 1.7)

25 Mw 30,000
(PDI 2.9)

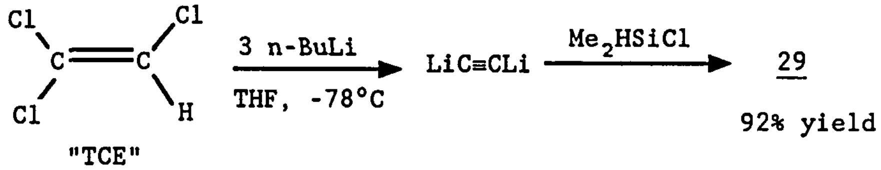
31 Mw 20,000
(PDI 2.2)

The usual method to synthesis polysilanes is Wurtz coupling[26] using dichlorosilanes and sodium. This approach can be modified to produce silicon-acetylene polymers by using an acetylene substituted on both ends with a chlorosilyl group. Thus, the reaction of bis(chlorodimethylsilyl)acetylene 30 and sodium sand in xylene afforded disilylene-acetylene polymer 26 with Mw ca. 10,000. The synthesis of bis(dimethylsilyl)acetylene

$$\underset{\underline{29}}{HMe_2Si\text{-}C{\equiv}C\text{-}SiMe_2H} \xrightarrow{CCl_4} \underset{\underset{95\%}{\underline{30}}}{ClMe_2Si\text{-}C{\equiv}C\text{-}SiMe_2Cl}$$

$$\underline{30} \xrightarrow[\text{xylene}]{Na} \underline{26}$$

29 could be accomplished in only 21% yield by using a literature procedure[27] in which dibromomagmesium acetylide and dimethylchlorosilane were used. In our studies trichloroethylene (TCE) was used as an acetylide precursor. Reaction of TCE with three equivalents of



n-BuLi quantitatively produced dilithium acetylide, which was quenched by dimethylchlorosilane.

Thermal properties of polymers 24, 25, 26 and 31 were investigated by thermogravimetric analysis (TGA) in argon or helium atmospheres. The volatile components extruded during pyrolysis were analyzed in a separate system composed of a vacuum pyrolysis tube connected to a quadrupole mass spectrometer either directly or via a gas chromatograph. The analysis results indicated that no volatile silicon- containing components were generated during pyrolysis. Figures 1-4 are TGA curves for these polymers at heating rate 20°C/min.

Basically no weight loss was detected up to 300°C. After that a weight loss at a moderate rate occurred and was essentially completed by 670°C to 750°C. Polymer <u>26</u> started to decompose at ca. 350°C which is significantly lower than polymer <u>24</u> where it started at ca. 450°C. This behavior is probably due to the weak Si-Si bond in <u>26</u> since scission of this bond would occur and initiate the decomposition process at lower temperature.

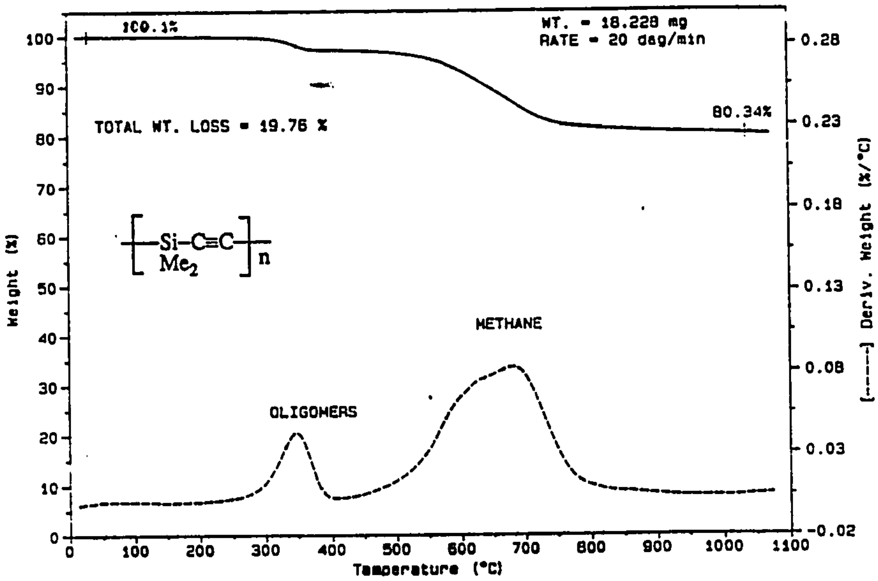


Figure 1. TGA curve of poly(dimethylsilacetylene) <u>24</u>

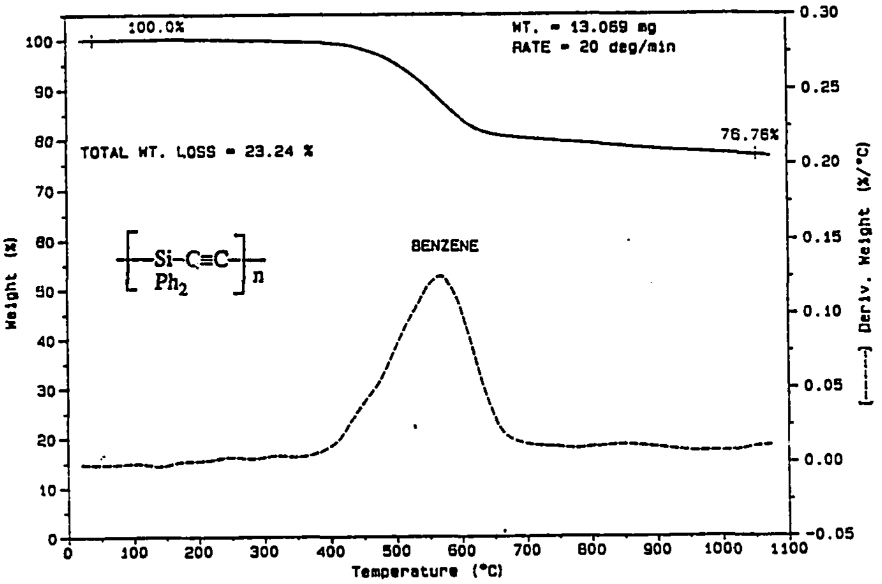


Figure 2. TGA curve of poly(diphenylsilacetylene) <u>25</u>

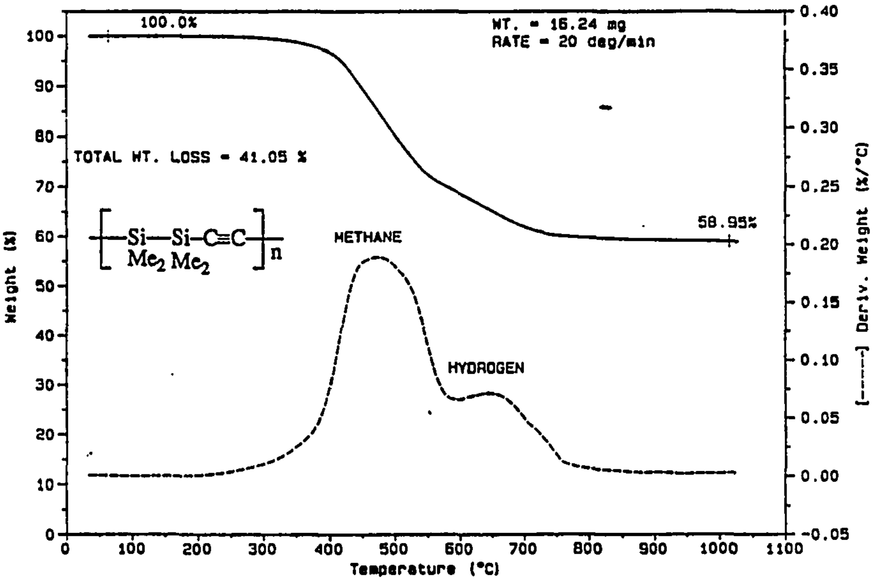


Figure 3. TGA curve of poly(tetramethyldisilanylene-acetylene) <u>26</u>

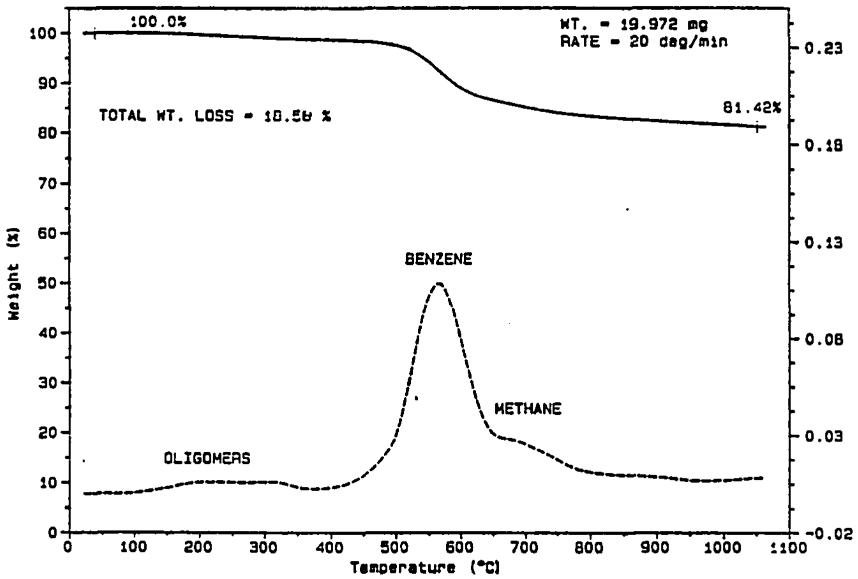


Figure 4. TGA curve of poly(methylphenylsilacetylene) 31

The nonvolatile chars obtained after the pyrolysis were all black, indicating that some free carbon was present. This was confirmed by elemental analysis for Si and C. X-ray powder diffraction, shown in Figure 5, revealed the pattern for SiC crystal.

Observed yields of SiC (after correction for excess C) are shown in Table 2. Theoretical maximum yields are based on complete retention of all Si atoms. Percentages of SiC in the char were calculated from elemental analysis data of the char where percentage of carbon in the chars were analyzed. SiC yields were obtained from the product of char yield and corresponding SiC content in the char.

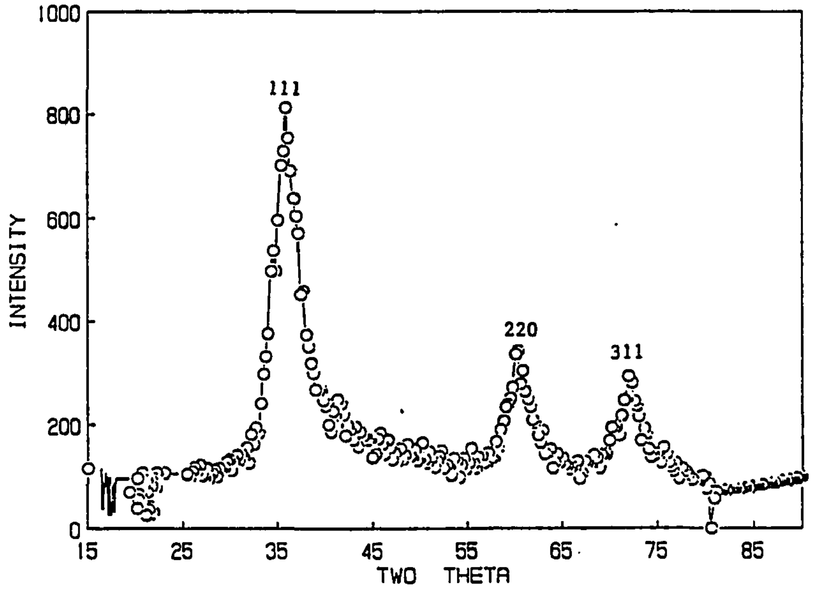


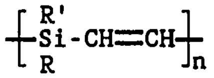
Figure 5. X-ray diffraction pattern for SiC powder produced by pyrolysis of polymer 26

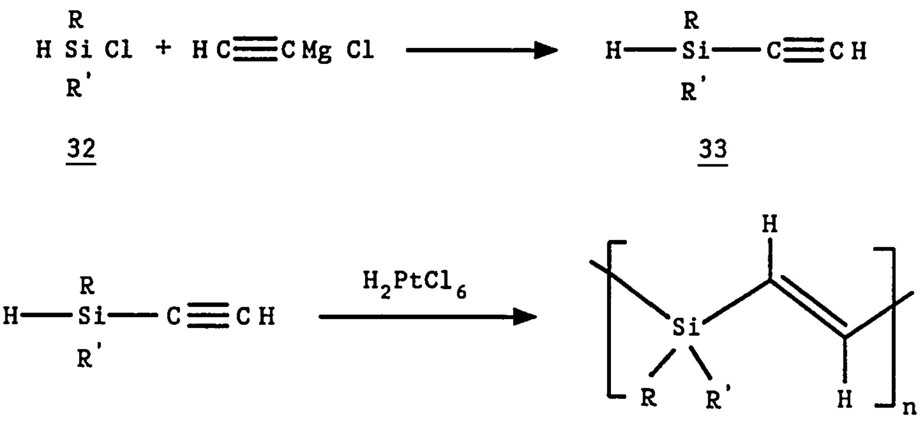
Table 2. SiC yields for poly(diorganosilacetylene)s

Polymer	Theoretical SiC yield (wt%)	Char yield (wt%)	SiC % in Char (wt%)	SiC yield (percent of theoretical)
$\left[\overset{\mathrm{Me_2}}{\mathrm{Si}}\mathrm{C{\equiv}C}\right]_n$	48.78	80.34	59.60	98.16
$\left[\overset{\mathrm{Me_2}}{\mathrm{Si}}-\overset{\mathrm{Me_2}}{\mathrm{Si}}\mathrm{C{\equiv}C}\right]_n$	57.14	58.95	70.90	73.14
$\left[\overset{\mathrm{Ph_2}}{\mathrm{Si}}\mathrm{C{\equiv}C}\right]_n$	19.42	76.76	29.00	114.5(?)
$\left[\overset{\mathrm{Ph}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{C{\equiv}C}\right]_n$	27.78	81.42	35.50	104.05

From Table 2, it is clear that apparent SiC yields are very high in the poly(diorganosilacetylene) system. Comparison with polysilanes which have SiC yields ranging from 1.2-54.5% (see Table 1), revealed that introduction of acetylenic units in the polysilane backbone offers the great advantage of retaining the silicon atom in the pyrolysis process.

Poly(diorganosilvinylenes) 13

The following route was designed to synthesize the polymer  $\left[\overset{R'}{\underset{R}{\mathrm{Si}}}\mathrm{-CH{=}CH} \right]_n$. The compound 33 was synthesized



32 33

33

34 R=R' = Me

35 R= Me, R' = Ph

by reaction of RR'SiHCl with HC≡CMgCl in very good yields(96% for R=Me, R'=Ph; 85% for R=R'=Me). In 33 a stoichiometric ratio between Si-H and acetylene functionalities is guaranteed to be fixed at 1:1. This ratio is very important to obtain high Mw polymer which can be shown in the following equation[28].

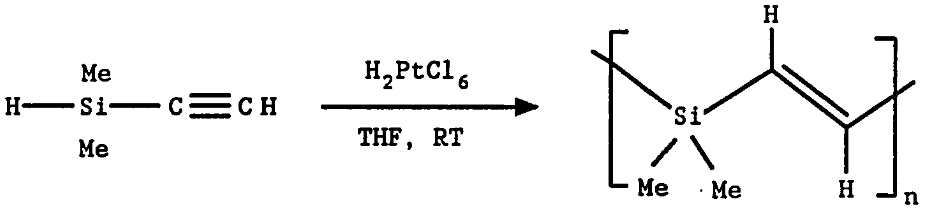
$$X_n = \frac{1 + r}{1 + r - 2rp} \qquad (1)$$

X_n is the number-average degree of polymerization, p stands for extent of reaction defined as a fraction of functionality converted during the reaction, and r is the stoichiometric imbalance between the two functionalities which is always defined so as to have a value equal to or less than unity. In our case

$$r = \frac{\text{number of Si-H functional groups}}{\text{number of HC}\equiv\text{C functional groups}}$$

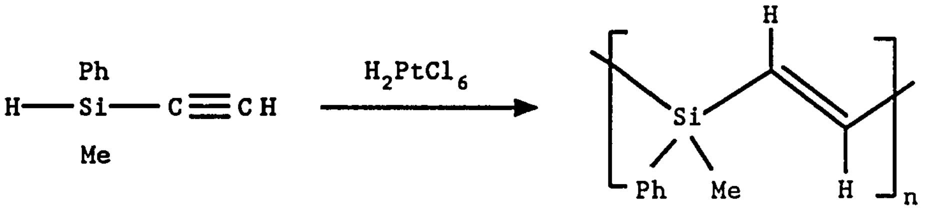
Since $r \leq 1$, $(1+r-2rp)$ will be larger than $(1+r-2p)$. From equation (1) it is clear that at same p value, X_n will reach maximum when stoichiometric imbalance r equals unity.

Bulk polymerization of dimethylethynylsilane 34 was performed in the presence of catalyst H_2PtCl_6. An explosive reaction was observed. The low boiling point of dimethylethynylsilane (below room temperature) made the bulk polymerization even more difficult to control. Solution polymerization in THF smoothly produced product with weight average Mw of 30,381 and polydispersity index (PDI) 4.8.



<u>34</u>,Mw 30,381

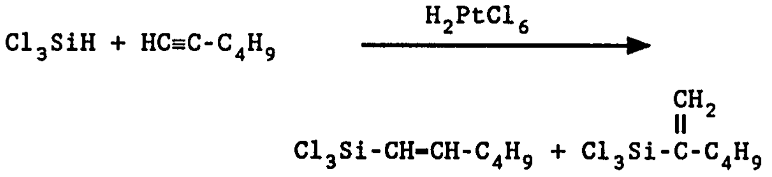
A vigorous exothermic reaction was also observed when ethynylmethylphenylsilane was mixed with a catalytic amount of H_2PtCl_6. A yellowish resin was obtained with



<u>35</u>

weight average Mw of 11,410 and polydispersity index (PDI) 2.5.

Hydrosilylation of monosubstituted alkynes often gives a mixture of α- and β-isomers[29] although the β-isomer always is predominant. For example[30] reaction



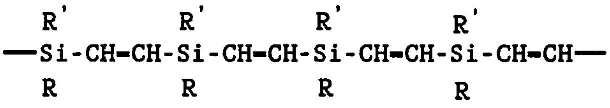
$$Cl_3SiH + HC{\equiv}C\text{-}C_4H_9 \xrightarrow{H_2PtCl_6} Cl_3Si\text{-}CH{=}CH\text{-}C_4H_9 + Cl_3Si\text{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}\text{-}C_4H_9$$

β-isomer α-isomer

<u>36</u> <u>37</u>

of trichlorosilane with 1-hexyne produces <u>36</u> and <u>37</u> in a ratio of 82 to 18. In the NMR spectra of polymers <u>34</u> and

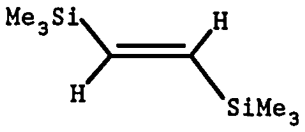
35, however, only one sharp resonance signal in the ^{29}Si NMR spectrum (Figure 6) and one singlet vinyl carbon signal at ca. 150ppm in the ^{13}C NMR spectrum (Figure 5) were observed. This result suggests a regular structure, i.e., head-to-tail chain sequence as shown in 38, was developed during the polymerization.



$$-\underset{R}{\overset{R'}{Si}}-CH{=}CH-\underset{R}{\overset{R'}{Si}}-CH{=}CH-\underset{R}{\overset{R'}{Si}}-CH{=}CH-\underset{R}{\overset{R'}{Si}}-CH{=}CH-$$

38

The abnormal down-field chemical shift of the vinyl carbon in the ^{13}C NMR spectrum is consistent with the value reported in the literature[31]. For example the observed ^{13}C chemical shift value of the vinyl carbon in the compound 39, 1,2-ethenediylbis(trimethyl)silane, is 150ppm.



39

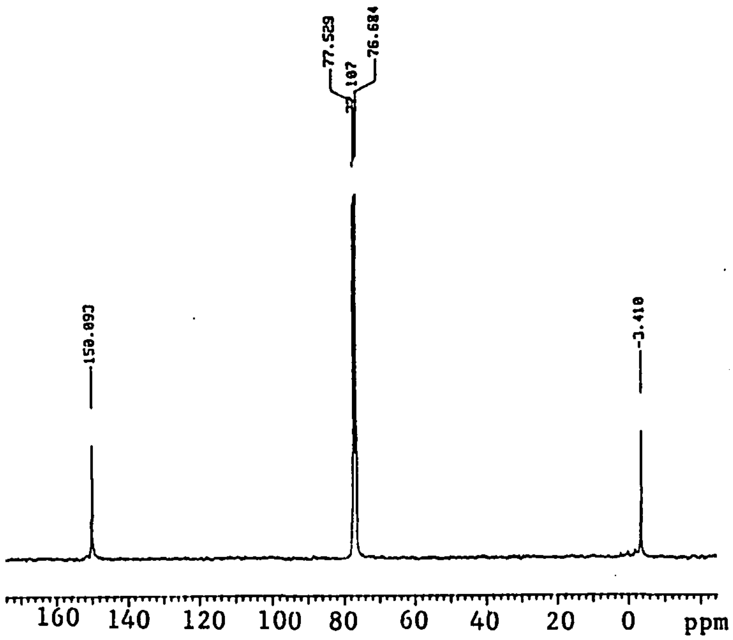


Figure 5. Gated Decoupling ^{13}C NMR of Polymer <u>34</u>

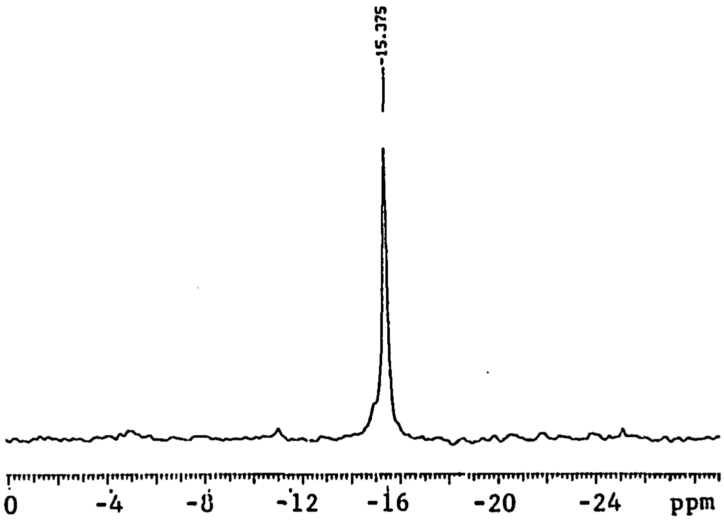
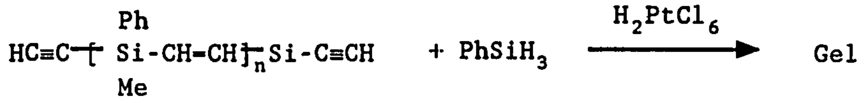


Figure 6. Gated Decoupling ^{29}Si NMR of Polymer <u>34</u>

Both poly(dimethylsilvinylene) 34 and poly(methylphenylsilvinylene) 35 have very good solubility in common organic solvents like benzene and THF. Poly(methylphenylsilvinylene) 35 can be easily spun into fiber and cast into film. These properties are very useful for application in ceramics.

During the effort to increase the molecular weight of poly(methylphenylsilvinylene) 35, no improvement was made by changing solvent (benzene and THF) and different length of reaction time. Analysis of IR spectra of polymer 35 and the corresponding monomer revealed that a small amount of excess acetylene (very weak absorptions at 2039 cm^{-1} and 3291 cm^{-1}) was present in the polymer product. No Si-H bond was detected in the polymer by IR and ^1H NMR. These results suggest that the stoichiometric ratio between Si-H bond and HC≡C- was lost during the reaction, and the end groups in the polymer were HC≡C-. This is probably caused by the reaction of Si-H with the catalyst $H_2PtCl_6.6H_2O$[32] and any residual moisture in the reaction flask. Thus, addition of a



$$HC\equiv C\left[\overset{Ph}{\underset{Me}{Si}}-CH=CH\right]_n Si-C\equiv CH \quad + PhSiH_3 \xrightarrow{H_2PtCl_6} Gel$$

40 (95%) 41 (5%) 42

Mw = 5676, PDI = 2.49

small amount of phenylsilane 41 to polymer 40 afforded a slightly cross-linked, transparent gel 42 after the mixture was heated to 120°C for 30 min. ^{13}C NMR spectrum of the polymer gel 42 was same as the linear polymer 35. However in ^{29}Si NMR spectrum three peaks were observed as shown in Figure 7. The resonance signal at -19 ppm is

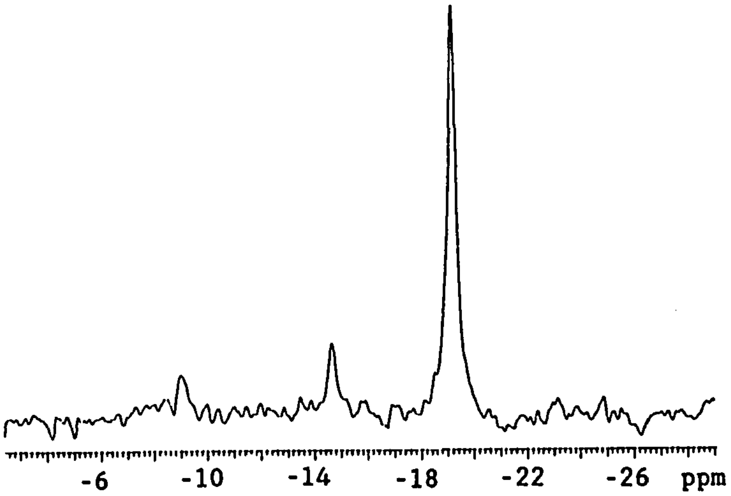
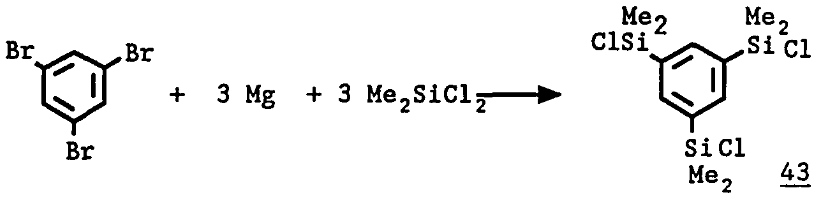


Figure 7. Gated Decoupling ^{29}Si NMR of Polymer 42

is due to the linear chain segment. The other two peaks are associated with the reaction product of phenylsilane since ^{29}Si chemical shift for $PhSiH_3$ is -59.6ppm (literature value -60.1ppm[33]).

1,3,5-Tris(dimethylsilyl)benzene 44 was also found to be an efficient crosslinking reagent for poly(diorganosilvinylene). The compound 44 was synthesized according to the following reaction. Synthesis of 1,3,5-tris(chlorodimethylsilyl)benzene[34] 43, was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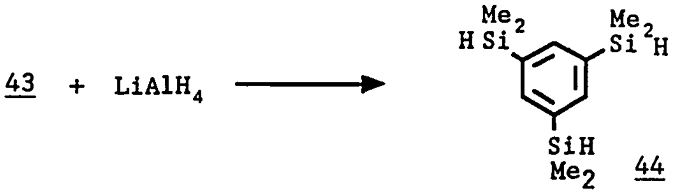
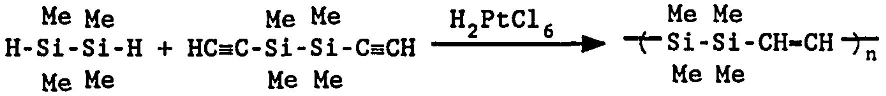

44

accomplished according to the literature procedure. Compound 43 was then reduced by $LiAlH_4$. Reaction of 5-10% compound 44 with poly(dimethylsilvinylene) in the presence of a catalytic amount of H_2PtCl_6 at 120°C led to an infusible solid in less than one minute!! The same result was also observed when poly(methylphenylsilvinylene) was used. Interestingly the crosslinked poly(dimethylsilvinylene) or poly(phenylmethylsilvinylene) did not change its original shape upon pyrolysis up to 1150°C. The chars obtained were oxidative stable.

In an effort to increase the silicon content in the polymer backbone, polymerization of disilane monomers 1,1,2,2-tetramethyldisilane 45 and 1,2-diethynyltetramethyldisilane 46 was studied. In contrast to the monosilane monomer $H-SiR_2-C\equiv CH$, refluxing of disilanes 45 and 46 in the presence of H_2PtCl_6 for overnight lead to no polymerization. Although it was reported that bubbling of oxygen[35] could enhance hydrosilylation of unactivated silanes with alkenes, no improvement was observed with bubbling oxygen in this case. Surprisingly, after two weeks stay at room temperature,



$$\text{H-}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{-}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{-H} + \text{HC}\equiv\text{C-}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{-}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{-C}\equiv\text{CH} \xrightarrow{H_2PtCl_6} \left(\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{-}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{-CH=CH} \right)_n$$

<u>45</u> <u>46</u> <u>47</u>

the reaction mixture gradually became an intractable pale yellow solid <u>47</u>. Solid state ^{13}C NMR (CPMAS) showed no acetylenic carbon but one broad vinyl carbon centered at 150 ppm. The ^{29}Si NMR spectrum (CP/MAS) revealed three sharp resonance signals at 7.95, -5.47 and -22.25 ppm with a ratio of ca. 1:1:2. The infrared spectrum showed a strong Si-O absorption at ca. 1000 cm^{-1}. The reason why polymer <u>47</u> is insoluble remains a question.

Thermal properties of polymers <u>34</u> and <u>35</u> were characterized by TGA under an argon flow at a heating rate of 20°C/min. The TGA curves for these polymers are shown in Figures 8, 9 and 10. Examination of the TGA curves for poly(diorganosilvinylene) polymers revealed that initial onset of decomposition started at ca. 300°C and the maximum rates of decomposition were between 450-500°C. This temperature was significantly lower than the corresponding poly(silylene-acetylene) polymers where the maximum rate of the decomposition was reached at ca.

550-650°C.

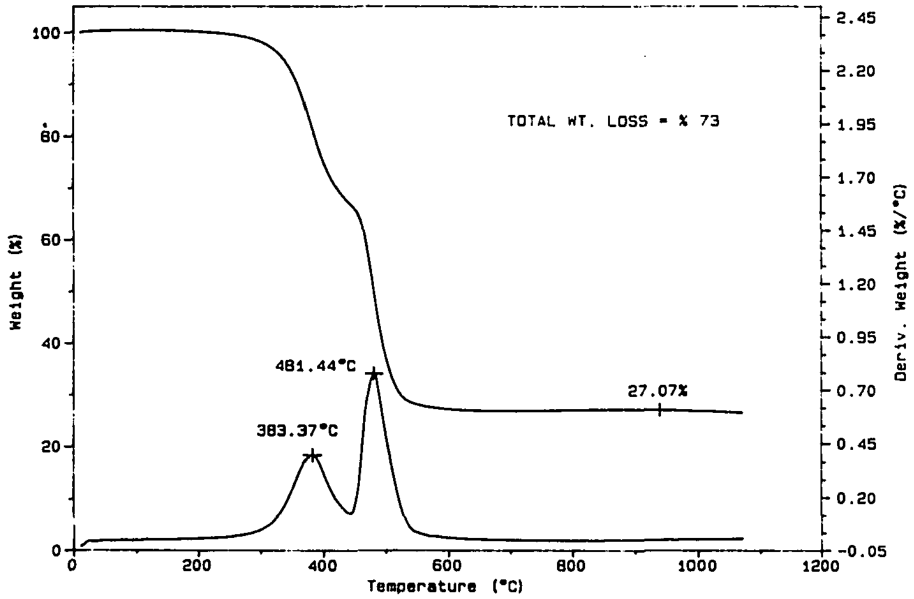


Figure 8. TGA curve of poly(dimethylsilvinylene)

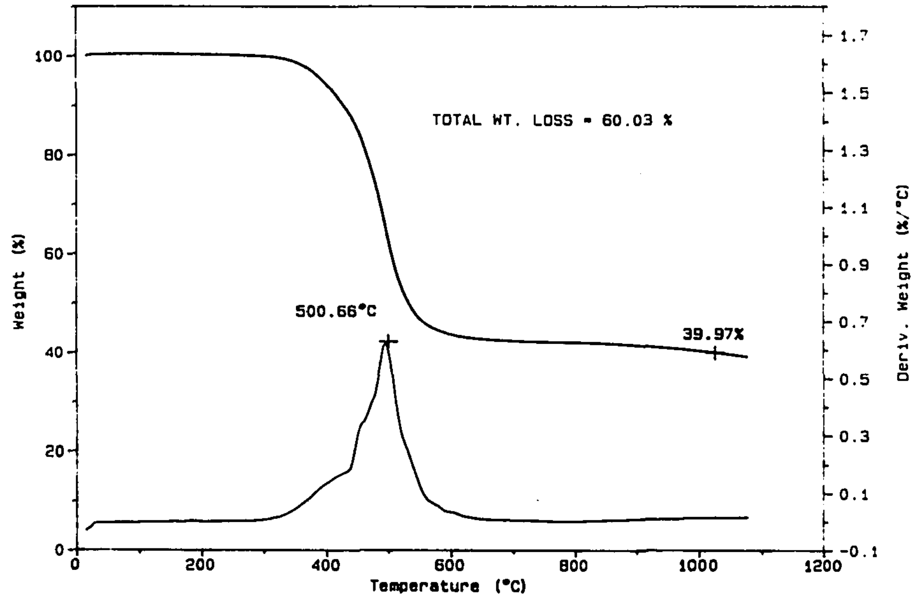


Figure 9. TGA curve of poly(phenylmethylsilvinylene)

The nonvolatile char obtained after the pyrolysis were black which is indicative of the free carbon in the char. The char was oxidative stable up to 1200°C in the air. X-ray powder diffraction (Figure 10) revealed the pattern for SiC crystalline SiC.

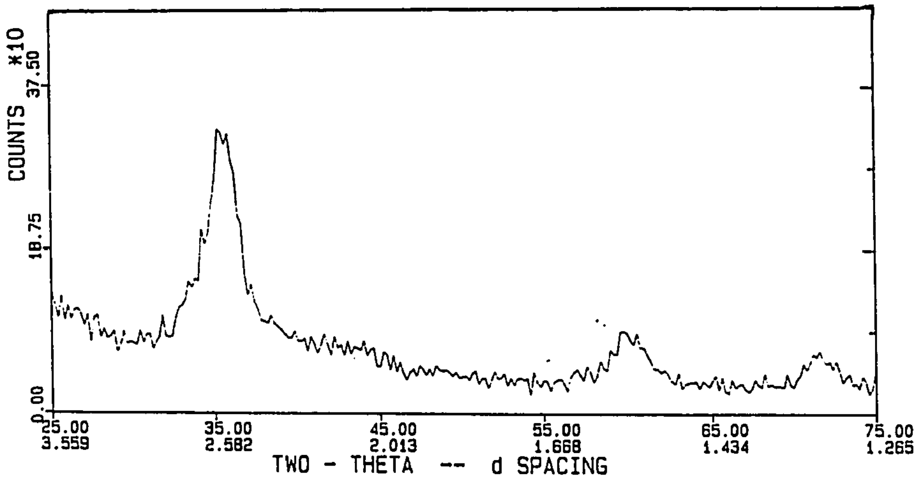


Figure 10. X-ray diffraction pattern for SiC powder produced by pyrolysis of poly(dimethylsilvinylene) 34 to 1300°C

The volatile decomposition products during the pyrolysis were determined by an on-line quadrupole mass spectrometer. Quantitative characterization of the freezable decomposition components was accomplished by trapping the volatile products in a cold finger and then analyzed by GC-MS. Analysis of the pyrolysis product from poly(phenylmethylsilvinylene) at ca. 450-550°C showed 54% benzene, 14% toluene, 6% ethylbenzene, 13% dimethylphenylsilane and some other minor uncharacterized products.

Pyrolysis of poly(dimethylsilvinylene) exhibited an unusual behavior. The char yield in the pyrolysis was not reproducible which varied from 15% to 42% (always lower than theoretical SiC yield 47.6%). Clearly some silicon was lost during the pyrolysis. In order to obtain more information about the pyrolysis process, the pyrolysis products were trapped by passing the pyrolysis gas through a cold finger at -78°C while poly(dimethylsilvinylene) was pyrolyzed at 450°C. The collected volatile product was analysed by a HEWLETT PACKARD model GC-IR-MS spectrometer (with HP 5970 series mass detector and HP 5965 infrared detector). The GC trace is shown in Figure 11. Most of the components contained silicon as

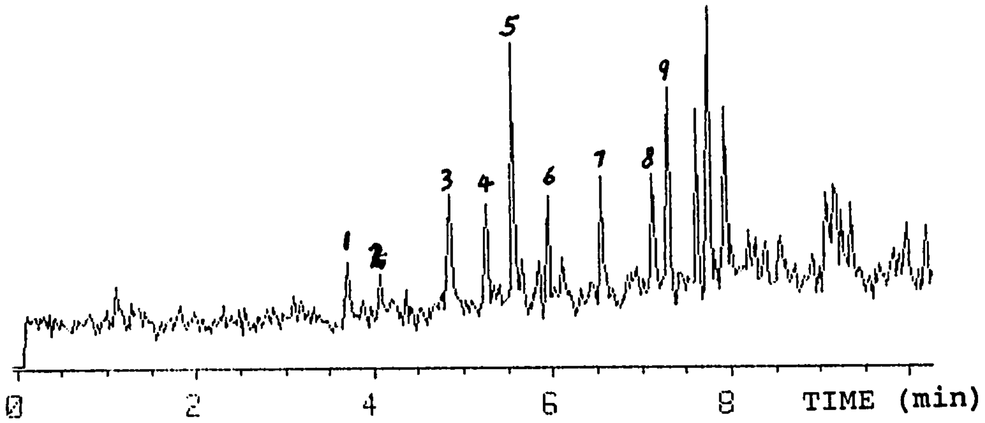
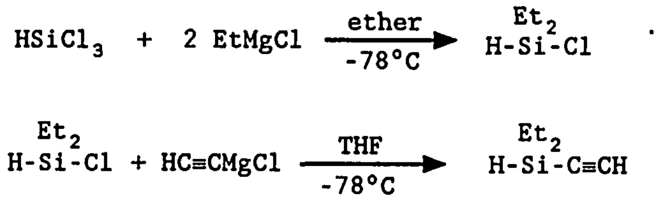


Figure 11. GC trace of the pyrogram at 450°C

indicated by the sharp strong $Si\text{-}CH_3$ absorption at 1256 cm^{-1} in their IR spectra. This observation explained the low char yield (lower than theoretical SiC yield) obtained in the pyrolysis of poly(dimethylsilvinylene).

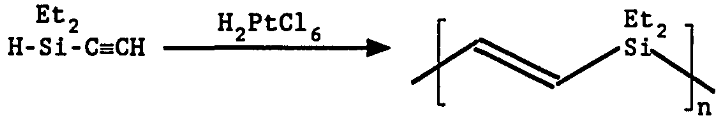
In the pyrolysis of poly(diorganosilvinylene)s there seemed to exist a competition between side group elimination and depolymerization of the polymer backbone. In order to examine the β-hydrogen effect of the side group toward the pyrolysis process, poly(diethylsilvinylene) <u>48</u> was sought. Trichlorosilane was reacted with two equivalents of ethylmagnesium chloride in diethylether, followed by quenching with ethynylmagnesium chloride to afford the desired monomer, diethylethynylsilane.



$$HSiCl_3 + 2\ EtMgCl \xrightarrow[-78°C]{ether} H\text{-}\overset{Et_2}{Si}\text{-}Cl$$

$$H\text{-}\overset{Et_2}{Si}\text{-}Cl + HC{\equiv}CMgCl \xrightarrow[-78°C]{THF} H\text{-}\overset{Et_2}{Si}\text{-}C{\equiv}CH$$

Polymerization of diethylethynylsilane in the presence of chloroplatinic acid catalyst required harsher conditions (160°C for 9 hours) than in the case of dimethylethynylsilane and phenylmethylethynylsilane. Extended reaction time at 160°C for 15 hours led to an insoluble product. Clearly the steric hindrance of the side group on silicon atom played an important role in this polymerization. The polymer 48 basically had a



48

regular structure as confirmed by its ^1H and ^{13}C NMR (Figure 12) spectra. It was an elastic, sticky resin and had a broad molecular distribution (Mw=110,700, PDI=36). The abnormally large polydispersity index (PDI) and multi-model in its GPC chromatogram (Figure 13) suggested the polymer might be branched although the branching mechanism was not clear. The minor absorption at ca. 148.5 ppm and 150 ppm in the ^{13}C NMR spectrum might be associated with this branching structure.

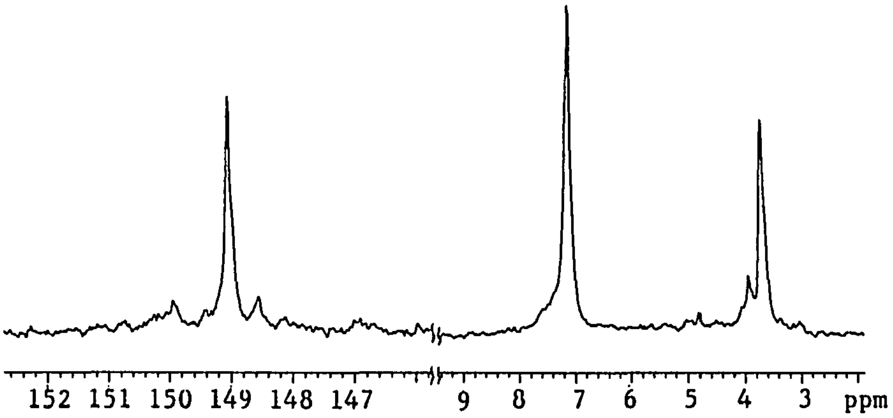


Figure 12. ^{13}C {H} NMR spectrum of poly(diethylsil-vinylene)

Decomposition of poly(diethylsilvinylene) was performed on a vacuum line which was coupled to a quadruple mass spectrometer. Ethylene started to be

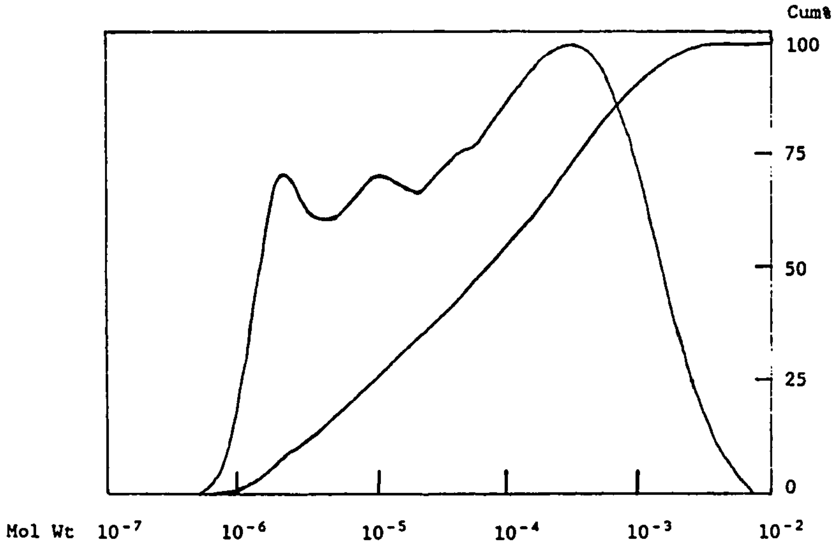


Figure 13. GPC chromatogram (molecular weight versus cumulative) of poly(diethylsilvinylene) 48 by using toluene as eluent and polystyrene as standard

formed at as low as 200°C. During the entire pyrolysis process from 200°C to 600°C, only ethylene (major), ethane (minor) and some hydrogen (started to be formed after 600°C) were detected as gaseous products. The char yield (from TGA), however, was ca. 17% which was lower than the theoretical char yield (35.7%). This was because some oligomer was formed during the pyrolysis.

In the ^{13}C NMR (Figure 14) spectra of the oligomer, only a broad resonance signal was detected. The disappearance of the double bond in the oligomer suggested that a more complicated process than simple depolymerization happened during the pyrolysis.

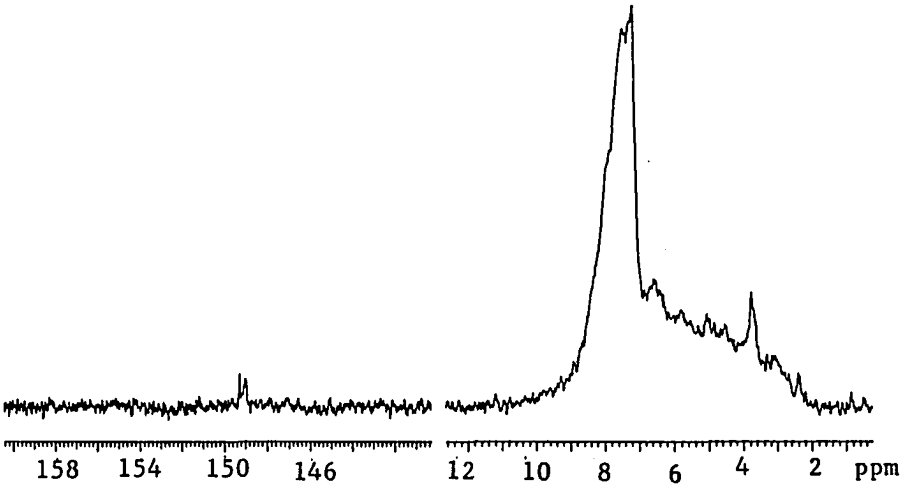
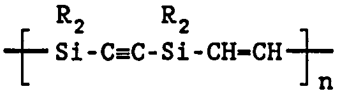


Figure 14. ^{13}C {H} NMR spectrum of the oligomer formed during the pyrolysis of poly(diethylsilvinylene)

Comparing the thermal properties of poly(diorganosilacetylene)s and poly(diorganosilvinylene)s, the former had a great ability to maintain the silicon during the pyrolysis although the char obtained in poly(diorganosilacetylene) seemed to be less oxidative stable than the one from poly(diorganosilvinylene). The incorporation of acetylene group into the backbone of poly(diorganosilvinylene) might improve the char yield. So the alternating copolymer, poly(diorganosilacetylene-alt-diorganosilvinylene) 49, was designed. In this polymer all silicon atoms are

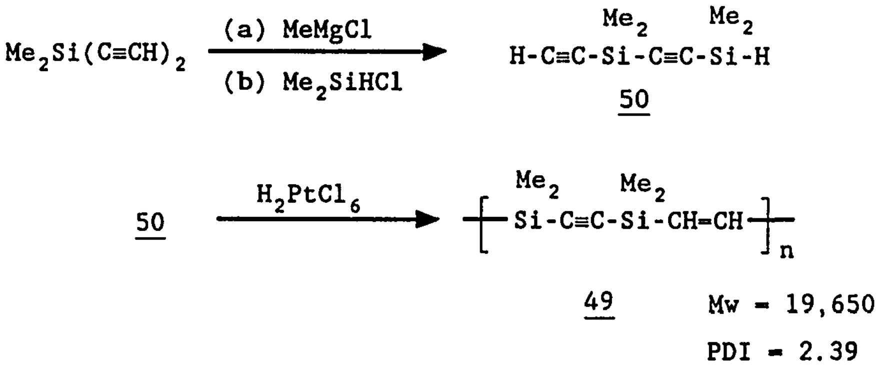


$$\left[\overset{R_2}{Si}-C\equiv C-\overset{R_2}{Si}-CH=CH \right]_n$$

49

connected to acetylene in order to increase the char yield during pyrolysis. Although unsaturated macrocyclic silicohydro-carbons[36] containing both -SiC≡CSi- and -SiCH=CH- units have been reported recently, no synthesis of polymer 49 was found in literature.

Polymer 49 was synthesized according to the following scheme. Diethynyldimethylsilane was reacted



$$Me_2Si(C\equiv CH)_2 \xrightarrow[(b)\ Me_2SiHCl]{(a)\ MeMgCl} H-C\equiv C-\overset{Me_2}{Si}-C\equiv C-\overset{Me_2}{Si}-H$$

50

$$\underline{50} \xrightarrow{H_2PtCl_6} \left[\overset{Me_2}{Si}-C\equiv C-\overset{Me_2}{Si}-CH=CH \right]_n$$

49 Mw = 19,650

PDI = 2.39

with one equivalent of methylmagnesium chloride, then was quenched with dimethylchlorosilane to afford compound 50.

As expected, polymerization of compound 50 was vigorously exothermic to give copolymer 49. The structure of the polymer was confirmed by ^{1}H, ^{13}C and ^{29}Si NMR spectra. The great selectivity of hydrosilation toward terminal acetylene was clearly seen in the ^{13}C NMR spectrum (Figure 15) of the polymer product.

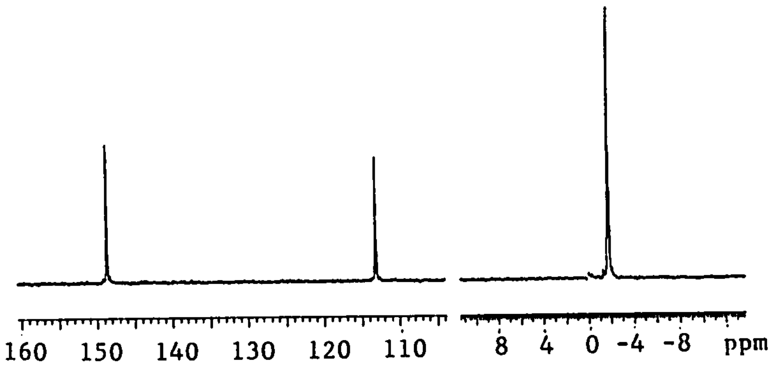


Figure 15. Quantitative ^{13}C{H} NMR spectrum of polymer 49

TGA curve of the poly(dimethylsilacetylene-alt-dimethylsilvinylene) was shown in Figure 16. Most of the decomposition was accomplished between 220-360°C. The decomposition temperature at maximum rate was as low as 300°C which is much lower than the one for both poly(dimethylsilacetylene) (650°C) and poly(dimethylsilvinylene) (488°C). As expected the char yield of the polymer was improved significantly (up to 33.9%) by introducing the acetylenic unit into the poly(dimethylsilvinylene). The char yield could be further increased to 39.7% by crosslinking the polymer with 10% 1,3,5-tris(dimethylsilyl)benzene prior to pyrolysis. Even more interestingly the char obtained from the polymer was oxidatively stable up to at least 1200°C. The oxidative stability above 1200°C was not examined.

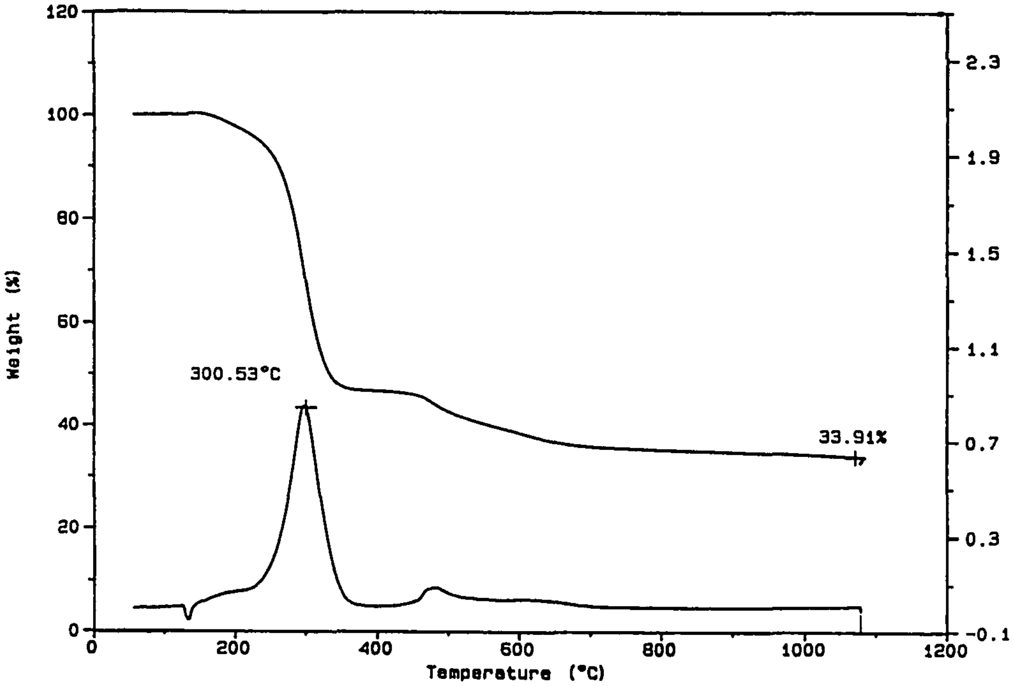


Figure 16. TGA curve of polymer 49

CONCLUSIONS

In conclusion, several poly(diorganosilacetylene) polymers have been synthesized via sodium coupling of $Cl(Me_2)SiSi(Me_2)Cl$, condensation of dichlorosilanes with acetylene diGrignard derivatives and dilithium acetylide. Among these synthetic routes, the dilithium acetylide method affords the highest molecular weight.

Poly(diorganosilacetylene) polymers have very high char yields after high-temperature pyrolysis. In contrast to polysilanes polymer (more than 50% silicon components lost during pyrolysis), no volatile silicon component is formed during the pyrolysis with poly(diorganosilacetylene). The ability of this type of polymer to retain silicon atoms at high temperature (≥1200°C), together with their better processabilities (compared with polysilanes) makes them potentially useful SiC precursors.

Several new poly(diorganosilvinylene) polymers have also been synthesized via hydrosilation of diorganoethynylsilanes. This polymerization process has advantage of easy operation and control. Spectral analyses (^{13}C and ^{29}Si NMR) have established the head-tail chain sequence in the polymers.

In addition to good solubility of the polymer, poly(diorganosilvinylene) has two other advantages.

First, no by-product is formed during the polymerization. This offers advantage of easy handling and processing. The common flow chart for polymer processing is:

Here monomer is first polymerized to form a polymeric product. If by-products are formed along with the polymerization, a tedious work-up procedure is often needed to separate the polymer before it can be used to make an object in usable forms or shapes like film, fiber, etc. So far all the preceramic polymers like polysilanes are formed via condensation of chlorosilanes with sodium or other metals. Copious amounts of salt are generated during this type of polymerization. For these polymers, purification must be performed prior to further use. In this aspect, the discovery of poly(diorganosilvinylene) polymers opens new opportunities to directly convert monomers into an object in a useful form.

Secondly, reaction conditions for hydrosilation is milder than for the Wurtz-coupling which is used in synthesis of polysilanes. Most functional groups can survive the conditions for hydrosilation This will allow us a wide choice to design functional polymers which would easily crosslink or would exhibit other interesting properties.

EXPERIMENTAL

Proton NMR spectra were obtained on a Nicolet NT-300 spectrometer. Carbon-13 and silicon-29 NMR spectra were acquired on a Varian VXR-300 spectrometer. In order to assure the quantitative feature of the ^{13}C and ^{29}Si spectra, ca. 0.02 M relaxation agent chromium(III) acetylacetonate was used in the $CDCl_3$ with relaxation delay 7 seconds for carbon and 9.6 seconds for silicon. All of the ^{13}C and ^{29}Si NMR spectra were taken under inverse gated decoupling condition.

Routine mass spectra were obtained on a Hewlett Packard 5970 GCMS operating at 70 ev.

Infrared spectra were obtained on an IBM IR-90 series FTIR spectrometer.

Molecular weight of the polymers were determined by gel permeation chromatography (GPC) with 6 Microstyragel columns in series of 500A, $2X10^3$A, $2X10^4$A, 10^5A. Toluene was used as eluent at a flow rate of 1.0 ml/min. The system was calibrated by polystyrene standards. The detection system used was a Waters Associates differential refractometer.

All solvents were distilled over calcium hydride. Carbon tetrachloride was distilled from phosphorus pentoxide. Methylmagnesium chloride and n-butyllithium were received from Aldrich.

Condensation of ClMgC≡CMgCl with R_2SiCl_2

A 50 mL 3-necked flask was equipped with a reflux condenser, a gas inlet and an outlet, and a mechanical stirrer. To the flask was charged with methylmagnesium chloride (21.3 mmol) and anhydrous THF (15 mL). The solution was heated to 50°C while a vigorous stirring was maintained. The acetylene gas, which was purified by passing through two dry-ice cold traps, was then introduced at such rate that temperature of the solution remained between 50-55°C. The introduction of the gas was stopped when the temperature of the solution dropped to 40-45°C (without external cooling), or when a jelly-like suspension occurred. The jelly-like suspension was then heated for an additional 2 hours at 55-60°C with a flow of N_2.

To the suspension prepared above, freshly distilled R_2SiCl_2 (10.65 mmol) or $ClMe_2SiSiMe_2Cl$ was added dropwise. The addition rate was controlled to maintain the temperature below 65°C. The suspension disappeared gradually. After the addition the mixture was heated to 65°C for an additional 3 hours. The mixture was then cooled to room temperature and subsequently poured into 20 ml dilute ice-cold aqueous HCl solution. Then 20 ml THF was added to help dissolve the polymers. After vigorous shaking, the organic layer was separated and further washed twice with dilute aqueous HCl solution. Finally the organic layer was dried over anhydrous Na_2SO_4. After precipitation from methanol solids with color ranging from pale yellow to reddish were obtained in ca. 50-60% yield.

Spectral properties:

$[SiMe_2C{\equiv}C]_n$: GPC Mw=3000. ^1H NMR ($CDCl_3$, 300 MHz) 0.4(broad). ^{13}C NMR ($CDCl_3$, 75.429 MHz) 0.1 ppm(2C, Si-Me) and 111.1ppm (2C, acetylenic). ^{29}Si NMR ($CDCl_3$, 59.595 MHz) -41.3ppm.

$[SiPh_2C{\equiv}C]_n$: Mw=4000. ^1H NMR ($CDCl_3$, 300 MHz) 7.2-7.4(3H) 7.7-7.8(2H). ^{13}C NMR ($CDCl_3$, 75.429 MHz) 111.4 (2C, acetylenic); 128.2 (2C), 130.5 (1C), 131.5 (1C) and 135.0 (2C) (phenyl carbons). ^{29}Si NMR ($CDCl_3$, 59.595 MHz) -49.6.

$[SiMe_2SiMe_2C{\equiv}C]_n$: Mw=4000. ^{13}C NMR ($CDCl_3$, 75.429 MHz, The spectrum was taken at 60°C due to the poor solubility of the polymer at room temperature. 117.0 (2C, acetylenic) and -2.9 (4C, Si-Me). ^{29}Si NMR ($CDCl_3$, 59.595 MHz, 60°C) -38.4.

Synthesis of Dimethyldiethynylsilane

Dimethyldiethynylsilane was prepared in a similar procedure as described in literature[37] (yield 42.5%) but with improved yield (85%).

HC≡CMgCl was prepared by using a similar procedure reported in literature[38]. A 2L oven-dried, three-necked, round-bottomed flask was equipped with a magnetic stirring bar, a graduated pressure-equalizing addition funnel, a gas inlet and an outlet. The flask was charged with 500 mL anhydrous THF. Acetylene (purified by passing through two dry-ice traps) was bubbled through the solvent for half hour. During the bubbling the flask was cooled by an ice-water bath. Then 1.62 moles of MeMgCl (3 M in THF) was added dropwise through the addition funnel with a rapid flow of acetylene. The addition rate of MeMgCl was controlled slowly enough to maintain the temperature below 10°C. After the addition was finished, bubbling of acetylene was maintained for an hour while the solution remained to be cooled by an ice-water bath.

The ethynylmagnesium chloride solution prepared above was cooled to -78°C by a dry-ice bath. Dimethyldichlorosilane (91 mL, 0.8 mol) was added dropwise into the ethynylmagnesium chloride suspension. After addition the dry-ice bath was removed and the reaction mixture was gradually warmed to room temperature overnight.

The reaction mixture was cautiously poured into 500 mL cold dilute aqueous HCl solution (0.2 M). The organic layer was separated and continuously washed by 0.2 M aqueous HCl solution until a constant volume was reached (ca. 30 times of washing). Fractional distillation through a 25 cm helices packed column gave dimethyldiethynylsilane as a colorless liquid, bp 86-87°C/760 mmHg, in 85% yield (purity 99%). The product had the following spectral properties. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.466 (s, 2H); 0.356 (s, 6H). Mass spectrum 108 (13) M^+; 93 (100) M^+-15; 77 (12); 53 (52).

Syntheses of Diphenyldiethynylsilane

Experimental procedure was the same as in synthesis of dimethyldiethynylsilane except the final work-up and purification steps. Here the reaction mixture from ethynylmagnesium chloride and diphenyldichlorosilane was cautiously poured into 0.2 M HCl aqueous solution. The organic layer was separated and was washed two more times with 0.2 M HCl aqueous solution. The organic layer was dried over anhydrous sodium sulfate. Most of the THF solvent was removed by rotatory evaporator. Vacuum distillation gave a colorless viscous liquid which quickly solidified to a white solid, mp 45-46°C, in 97% yield (purity 100%). The product had the following spectral properties. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.739 (s, 2H); 7.35-7.43 (m, 6H); 7.73-7.78 (m, 4H). Mass spectrum 232 (52) M^+; 231 (100) M^+-1; 207 (2) M^+-25; 205 (11); 178 (15); 155 (37); 129 (59); 103 (33); 77 (30); 53 (77).

Condensation of $ClMg-C{\equiv}C-SiMe_2-C{\equiv}C-MgCl$ with Me_2SiCl_2

To a 100 mL three-necked flask, equipped with a mechanical stirrer and a condenser, was added anhydrous THF (42 mL) and 60 mmol MeMgCl (3 M solution in THF, 20 ml, 60 mmol). Dimethyldiethynylsilane (3.42 g, 30 mmol) was added dropwise through a syringe while the flask was cooled by an ice-water bath. When the reaction was subsided down (no more gas evolved), the ice-water bath was removed. The mixture was heated at 50°C for four hours. Then dimethyldichlorosilane (3.6 mL, 30 mmol) was added dropwise through a syringe at room temperature while the reaction mixture was stirred vigorously. After the addition the mixture was stirred at 50°C overnight. A viscous mixture was obtained. The mixture was cooled by an ice-water bath, and 30 mL cold dilute aqueous HCl solution was added. The organic layer was separated and further washed five times with dilute aqueous HCl solution in order to completely remove the salts. After precipitation out of methanol, a pale yellowish solid (4.12 g, yield 78%) was obtained with molecular weight 4000.

Condensation of $ClMg-C\equiv C-SiPh_2-C\equiv C-MgCl$ with Ph_2SiCl_2

Diphenyldiethynylsilane (2.234 g, 10 mmol) was dissolved in 10 mL anhydrous benzene in a 25 mL, three-necked flask equipped with a condenser and a mechanical stirrer. Methylmagnesium chloride (6.67 mL, 3 M in THF solution, 20 mmol) was added dropwise into the solution while the flask was cooled by an ice-water bath. After the reaction was subsided down, the mixture was stirred at room temperature for an half hour, at 50°C for one hour. The solution became more and more viscous and the stirrer was difficult to move. Additional 10 ml benzene was added in order to reduce the viscosity of the solution. Then diphenyldichlorosilane (2.1 mL, 10 mmol) was added dropwise through a syringe. The solution was stirred at 50°C overnight. The reaction mixture was cooled by an ice-water bath. Then 10 mL cold dilute aqueous HCl solution was added. After stirring for a while the organic layer was separated and further washed five times with dilute aqueous HCl solution. Finally the organic layer was dried over anhydrous Na_2SO_4. After precipitation by adding to methanol a pink solid (3.82 g, yield 92%) was obtained with Mw 5000.

Dehydrocondensation of diethylsilane with dimethyldiethynylsilane in presence of H_2PtCl_6/I_2

To a oven-dried 25 mL flask equipped with a magnetic stir bar was added diethylsilane (0.88 g, 10 mmol), dimethyldiethynylsilane (1.08 g, 10 mmol) and anhydrous benzene (4 mL). Then H_2PtCl_6 (0.1 mL, 0.05 M solution in THF) and iodine (0.13 g in 1 mL benzene) was added into the reaction mixture by a syringe. As soon as the catalysts was added some gas was evolved from the reaction mixture. However it quickly subsided down in about one minute. The mixture was stirred overnight. No polymer was found in the product mixture. Analysis of the product by GC-MS showed the major components in the mixture were starting materials.

Synthesis of bis(dimethylsilyl)acetylene (29)

To a 1000 mL oven-dried, three-necked, round-bottomed flask, equipped with a magnetic stir bar and a pressure-equalizing graduated addition funnel, was added 180 mL anhydrous THF. The system was flushed with N_2. The flask was cooled down to -78°C and n-butyllithium (2.0 M in hexane, 320 ml, 0.8 mol) was added. Trichloroethylene (24 mL, 0.266 mol) was added slowly dropwise through the addition funnel at -78°C while an efficient stirring was maintained. The addition lasted about 30 minutes. After the addition the mixture was allowed to be gradually warmed to room temperature. A lot of white salts precipitated out during this period. Following continuous stir for an hour, the mixture was cooled back to -78°C and dimethylchlorosilane (70 ml, 0.64 mole) was added through the addition funnel (lasted ca. 15 min.). The mixture was continued to stir one hour at -78°C, two hours at room temperature. To the reaction mixture was added pentane (100 mL) and then cold water (200 mL). The organic layer was quickly separated and dried over anhydrous Na_2SO_4. Fractional distillation through a 25 cm helices packed column gave bis(dimethylsilyl)acetylene as a colorless liquid (35 g, yield 92%),bp 118-120°C/760 mmHg. The product had the following spectral properties. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.08 (septet, 2H, J=4 Hz) and 0.23 ppm (d, 12H, J=4 Hz). Mass spectrum 142 (2) M^+; 141 (9) M^+-H; 127 (100) M^+-Me; 83 (41); 73 (98); 43 (58).

Chlorination of bis(dimethylsilyl)acetylene

To a 250 mL round-bottomed, oven-dried flask which was equipped with a maganetic stir bar and a condenser, was added carbon tetrachloride (150 mL, distilled from P_2O_5), bis(dimethylsilyl)acetylene (26 g) and benzoylperoxide (2 g) in a nitrogen atmosphere. The solution was refluxed under the inert atmosphere until complete disappear of starting material from GC analysis (ca. 24 hours). Fractional distillation through a 25 cm helices-packed column gave bis(chlorodimethylsilyl)-acetylene as a colorless liquid (36 g, yield 94%), b.p. 100°C/85 mmHg. Mass spectrum of the product 214 (0.6) $M^+ +4$; 212 (3.0) $M^+ +2$; 210 (4.1) M^+; 197 (73) $M^+ +2-Me$; 195(100) $M^+ -Me$; 187 (10.7) $M^+ +2-Cl$; 185 (27.3) $M^+ -Cl$.

Coupling of bis(chlorodimethylsilyl)acetylene with sodium sand

To a 500 mL oven-dried, three-necked, round-bottomed flask which was equipped with a condenser, an addition funnel and a mechanical stirrer, was added anhydrous xylene (60 mL) and sodium metal (2 g, 0.087 mole) under a nitrogen atmosphere. The flask was heated to 120°C (oil bath temperature) for 20 minutes while the mixture was stirred vigorously. Then the temperature was cooled to 60°C and a fine sodium sand dispersion was formed. Bis(chlorodimethylsilyl)acetylene (6.5 g, 0.031 mole) was added through the addition funnel dropwise in ca. 20 minutes. After addition the mixture was stirred under gentle refluxing for two hours. Then 5 mL trimethylchlorosilane was added to remove the excess sodium. After additional stirring for five hours, the reaction mixture was transferred into a separation funnel and 50 mL Et_2O was added. The mixture was washed 10 times with dilute aqueous HCl solution (5%). The organic layer was dried over Na_2SO_4. Most of the sovent was removed on a rotatory evaporator. Precipation from methanol gave a white solid (1.5 g, yield 34%). GPC of the white solid showed a Mw of 10,000.

Preparation of dimethylethynylsilane (33)

In a 1000 mL oven-dried, three-necked flask ethynylmagnesium chloride (0.5 mole) was prepared following the same procedure as described in dimethyldiethynylsilane. To the suspension of the HC≡CMgCl was added dimethylchlorosilane (54 mL, 0.5 mol) dropwise at -78°C. After addition the temperature was gradually warmed to room temperature. The reaction system was closed by connecting to a balloon to avoid the loss of dimethylethynylsilane product. After the mixture was stirred at room temperature for two hours, the flask was cooled to 0°C by an ice-water bath. Then 200 mL dilute cold aqueous HCl solution (0.2 M) was added into the flask. As soon as the organic layer became clear, the mixture was poured into a separation funnel and the organic layer was separated. After drying over anhydrous sodium sulfate, dimethylethynylsilane was distilled through a 25 cm helices packed column. The receiver was cooled by a dry-ice bath. A colorless liquid (ca. 36 g, 85% yield, 94.5% pure by GC) was collected below 40°C. The product had the following spectral properties. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.13 (heptet, J=3.78 Hz, 1 H); 0.27 (d, J=3.86 Hz, 6 H); 2.4 (s, 1 H). Mass spectrum 84 (21) M^+; 83 (27) M^+-1; 69 (100) M^+-Me.

Polymerization of dimethylethynylsilane

A catalytic amount of H_2PtCl_6 was dissolved in 5 mL THF in a 50 mL flask equipped with a cold finger which was filled by dry-ice and isopropanal. Dimethylethynylsilane (10 mL) was added through a syringe dropwise into the solution. The reaction proceeded smoothly under a gentle reflux. The mixture was stirred overnight. After precipitation by adding to methanol (50 mL), a white solid (4.2 g) was obtained with softing point ca. 95-105°C. The polymer product had the following spectral properties. GPC Mw=30,381, PDI=4.82. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 ppm (s, 2H); 6.59 ppm (s, 6 H). ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ -3.41 ppm (2C) and 150.09 ppm (2C). ^{29}Si NMR ($CDCl_3$, 59.595 MHz) δ -15.37 ppm.

Preparation of phenylmethylethynylsilane

In a 500 mL oven-dried, round-bottomed three-necked flask, equipped with a magnetic stirring bar and a graduated pressure-equalizing addition funnel, $HC\equiv CMgCl$ (0.16 mol in 200 mL THF) was prepared according to the same procedure as described in dimethyldiethynylsilane. After $HC\equiv CMgCl$ was cooled down to -78°C, phenylmethylchlorosilane (25 g, 0.16 mol, received from Petrarch) was added dropwise into the mixture. After the addition, the temperature was allowed to raise gradually to room temperature and the mixture was stirred for two hours. Then the flask was cooled by an ice-water bath. To the suspension mixture, 100 mL hexane and 100 mL cold dilute aqueous HCl solution were added. As soon as the organic layer became clear, the organic layer was separated and dried over anhydrous sodium sulfate. Most solvent was removed by a rotatory evaporator. Fractional distillation through a 5 cm helices packed column gave a colorless liquid (21.3 g, yield 92%), b.p. 70-72°C/13 mmHg, purity 98% by GC. The product had the following spectral properties. Mass spectrum 147 (12) M^++1; 146 (65) M^+; 145 (100) M^+-H; 132 (14); 131 (91) M^+-Me; 120 (23); 105 (61); 77 (20); 68 (47) M^+-Ph. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.52 ppm (d, J=3.9 Hz, 3H); 2.55 ppm (s, 1H); 4.65 ppm (q, J=3.9 Hz, 1H); 7.30-7.75 ppm (m, 5H). IR (neat) υ 3231 (s), 3071 (m), 2913 (w), 2149 (s), 2039 (s), 1429 (s), 1254 (s), 1117 (s), 991 (vs), 937 (vs), 749 (s), 725 (s), 600(m) cm^{-1}.

Polymerization of phenylmethylethynylsilane

In a 25 mL oven-dried, round-bottomed flask which was equipped with a condenser and a magnetic stirring bar, a catalytic amount of H_2PtCl_6 was dissolved in 1 mL anhydrous THF. The solution was heated at 50°C and phenylmethylethynylsilane (4 mL, 3.2 g) was added dropwise at this temperature. The reaction was exothermic and the solution became more and more viscous as the polymerization carried on. After the reaction subsided down, the condenser was removed and the flask was fitted with a short path distillation apparatus. The solvent was distilled off and the viscous solution was heated at 120°C overnight. The solution became so viscous at this temperature that the stirring bar could not move. After cooling down to room temperature, a pale yellow transparent resin was obtained. GPC of the resin showed Mw=11,410, PDI=2.5. The polymer had the following spectral properties. ^1H NMR ($CDCl_3$, 300 MHz) δ -0.1-0.8 ppm (broad peak, 3H); 6.7-6.9 ppm (broad, 1H); 7.0-7.9 ppm (broad, 5H). ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 150.2 ppm (1C); 136.6 ppm (1C); 134.5 ppm (2C); 129.1 ppm (1C);

127.8 ppm (2C); -4.7 ppm (1C). ^{29}Si NMR (CDCl$_3$, 59.595 MHz) δ -19.3 ppm. IR (KBr pellet) ν 3271 (vw), 3067 (m), 3009 (m), 2035 (vw), 1427 (s), 1250 (s), 1173 (s), 1109 (s), 1013 (s), 791 (s), 733 (s), 696 (s), 471 (m) cm^{-1}.

Hydrosilylation of poly(phenylmethylsilvinylene) with phenylsilane

In a 25 mL flask, equipped with a magnetic stir bar, was added poly(phenylmethylsilvinylene) crude polymer (2.0 g) and phenylsilane (0.015 g). The mixture was a very viscous fluid at 120°C. After the mixture was heated to 120°C for 20 min., the mixture was solidified. The product swelled but not soluble in organic solvent like THF and chloroform.

Synthesis of 1,3,5-tris(dimethylsilyl)benzene (44)

In an oven-dried, argon-flushed 250 mL flask which was equipped with a magnetic stirring bar and a condenser, was added anhydrous THF (60 mL) magnesium turnings (3.5 g, 0.145 mol) and 1,3,5-tribromobenzene (9.0 g, 0.029 mol, received from Aldrich). The reaction was slowly started under stirring. The reaction was exothermic and occasional cooling was needed. After the reaction subsided the mixture was heated to reflux for another four hours. Then the salt and unreacted magnesium was removed by filtration. The organic solution was concentrated by distillation to 20 mL. Then this 1,3,5-tris(chlorodimethylsilyl)benzene solution was cooled by an ice bath, and lithium aluminum hydride (1.0 M solution in THF, 35 ml) was added dropwise via a syringe. After addition the mixture was stirred at room temperature overnight. To the product solution was added 100 mL hexane. Then the obtained solution was slowly poured into 50 mL cold dilute aqueous HCl solution. The organic layer was separated and dried over anhydrous sodium sulfate. Most of the solvent was removed on a rotatory evaporator. Vacuum distillation afforded a colorless liquid (1.2 g) b.p. 60-70°C/0.10 mmHg (literature value[39] b.p. 102°C/2.4 mmHg). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 ppm (s, 3H), 4.46 ppm (sept, J=3.6 Hz, 3H), 0.38 (d, J=3.6 Hz, 18H).

Crosslinking reaction between poly(dimethylsilvinylene) and 1,3,5-tris(dimethylsilyl)benzene

To a 5 mL oven-dried flask equipped with a magnetic stirring bar, was added poly(dimethylsilvinylene) (white powder 0.2 g), 1,3,5-tris(dimethylsilyl)benzene (0.01 g) and catalytic amount of H_2PtCl_6. The mixture was put in an oil bath which was preheated to 120°C. The mixture was melt first and then quickly solidified in less than one minute at 120°C.

Synthesis of diethylchlorosilane

In an oven-dried 2L flask, which was equipped with a magnetic stirring bar and an additional funnel, was charged with freshly distilled trichlorosilane (80.7 mL, 0.8 mol) and anhydrous diethyl ether (700 mL). The solution was cooled down to -78°C. Then ethylmagnesium chloride (1.6 mol in 800 mL diethyl ether, received from Aldrich) was added dropwise through the addition funnel at -78°C while an efficient stirring was maintained. After addition the mixture was stirred at -78°C for an hour, and then was gradually warmed to room temperature overnight. Most of the salt was removed by passing the reaction product mixture through a sintered glass filter. Distillation of the organic solution through a 25 cm column packed with glass helices, gave a colorless liquid (90 g, 90% pure by GC, yield 83%) at 100-101°C. Mass spectrum of the product: 124 (3.7) $M^{+}+2$; 123 (5.3) $M^{+}+1$; 122 (11.1) M^{+}; 121 (13.5) $M^{+}-H$; 96 (2.6); 95 (33.6); 94 (22.3); 93 (100) $M^{+}-C_2H_5$; 92 (46.2); 87 (6.8); 86 (2.3); 67 (15.9); 66 (4.5); 65 (53.2); 64 (6.7); 63 (23.5); 59 (4.6); 58 (4.3); 57 (2.9); 56 (1.5); 55 (3.2); 53 (3.5).

Synthesis of ethynyldiethylsilane

In a 2L oven-dried, three-necked, round-bottomed flask which was equipped with a magnetic stirrer, a gas inlet and an outlet, ethynylmagnesium chloride (0.7 mol) was prepared (by the same procedure as described in dimethyldiethynylsilane) from methylmagnesium chloride (0.7 mol) and acetylene in 900 mL anhydrous THF. After the ethynylmagnesium chloride solution was cooled to -78°C, diethylchlorosilane (90 g, 90% pure) was added dropwise through an additional funnel. After addition the mixture was stirred at -78°C for 20 min, then the temperature was gradually warmed to room temperature and the mixture was stirred overnight.

To another 2L flask which was equipped with a magnetic stirring bar and was cooled by an ice-bath, was charged with 300 mL dilute aqueous HCl solution and 200 mL pentane. Into this aqueous HCl solution, the above product solution was slowly added portion by portion. The organic layer was separated and was further washed once by cold dilute HCl aqueous solution. The obtained organic layer was dried over anhydrous sodium sulfate. Fractional distillation through a 45 cm column which was packed with glass helices gave 25 g colorless liquid, b.p. 98.5- 99°C/760 mmHg. The product was 97% pure by GC which was contaminated by 1.4% ethyldiethynylsilane and

1.6% triethylsilane. This product was used in the following polymerization studies. The low yield in this reaction was caused by the serious loss of the product during separation of impurities, i.e., triethylsilane (b.p. 107-108°C) and ethyldiethynylsilane. The product had the following spectral properties. Mass spectrum 108 (2.2) M^+; 107 (16.5) M^+-H; 106 (1.7); 105(1.9); 93 (4.4); 83 (1.5) M^+-C_2H; 82 (18.5); 81 (7.5); 80 (35.3); 79 (61.4) $M^+-C_2H_5$; 78 (12); 77 (17.2); 76 (2.3); 68 (1.1); 67 (12.6); 66 (3.5); 65 (2.2); 56 (2.0); 55 (9.1); 54 (23.1); 53 (100); 52 (4.9); 51 (1.4). IR (neat) ν 3307 (m), 2970 (m), 2179 (s), 2043 (m), 1344 (m), 973 (w), 818 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 3.93 ppm (d.quin., J_1=3.6 Hz, J_2=0.9 Hz, 1H), 2.39 ppm (d, J=0.9 Hz, 1H), 1.04 ppm (t, J=7.8 Hz, 6H), 0.70 ppm (d.q., J_1=7.8 Hz, J_2=3.3 Hz, 4H).

Polymerization of ethynyldiethylsilane in presence of chloroplatinic acid

In a 25 mL oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar and a condenser, the catalytic amount of chloroplatinic acid was dissolved in 0.2 mL anhydrous THF. The monomer (5 mL, 3.82 g) was added dropwise through a syringe. The solution was gradually warmed up. Then the mixture was heated at 120°C (oil bath temperature) for 6 hours. The solution was only slightly viscous. After the mixture was heated at 160°C for 9 hours, a viscous liquid at 160°C was obtained. This material was a sticky elastic resin at room temperature which was readily soluble in THF, $CHCl_3$ toluene. The polymer had the following spectral properties. GPC Mw 110,700, PDI=36. ^1H NMR ($CDCl_3$, 300 MHz) δ 6.598 (s, 1.727H), 6.395 (s, 0.273H), 0.921 (t, J=7.8 Hz, 6H), 0.635 (q, J=7.8 Hz, 4H). ^{13}C-{^1H} NMR ($CDCl_3$, 75.429 MHz) δ 149.06, 7.15, 3.75.

Synthesis of 2,5,5-trimethyl-2,5-disilahepta-3,5-diyne (50)

In a 500 mL oven-dried flask which was equipped with a magnetic stirring bar and an additional funnel, was added anhydrous THF (300 mL) and dimethyldiethynylsilane (50 g, 0.46 mol). After the solution was cooled to 0°C by an ice water bath, methylmagnesium chloride (3 mol solution in THF, 100 mL, 0.30 mol) was added dropwise through the addition funnel. The addition lasts about one hour. After the addition the solution was continued to stir at 0°C for an hour. Then the solution was cooled to -78°C by a dry-ice bath, and dimethylchlorosilane (30.3 g, 0.32 mol) was added. After stirring at -78°C for half hour, the mixture was gradually warmed to room temperature for overnight.

In another 1000 mL flask was added 200 mL dilute HCl aqueous solution and 200 mL pentane. After the HCl solution was cooled to 0°C, the product suspension was slowly poured into it portion by portion. The organic layer was separated, washed one more time by cold water and then dried over anhydrous sodium sulfate. Fractional distilation gave 2,5,5-trimethyl-2,5-disilahepta-3,5-diyne as a colorless liquid (38.1 g, yield 76.5%, 99.4% pure by GC), b.p. 86°C/64 mmHg. The product had the following spectral properties. Mass spectrum 166 (2.1) M^+; 165 (7.3) M^+-H; 153 (7.3); 152 (16.7); 151 (100) M^+-Me; 135 (3.1); 126 (2.1); 125 (3.4); 121 (2.4); 116 (3.7); 111 (13.3); 109 (3.1); 107 (4.5); 105 (2.8); 97 (12); 95 (2.9); 93 (13.8); 85 (3.3); 84 (5.0); 83 (54.7); 81 (7.8); 77 (2.8); 75 (4.4); 74 (4.9); 73 (63.8); 69 (8.7); 68 (6.6); 67 (15.7); 66 (5.1); 59 (2.9); 58 (3.1); 55 (12.1); 53 (22.2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.10 (septet, J=3.9 Hz, 1H), 2.46 (s, 1H), 0.35 (s, 6H), 0.24 (d, J=3.9, 6H).

<u>Polymerization of 2,5,5-trimethyl-2,5-disilahepta-3,5-diyne (50) in presence of H_2PtCl_6</u>

In a 25 mL oven-dried flask, which was equipped with a magnetic stirring bar and a condenser, catalytic amount of H_2PtCl_6 was dissolved in 5 mL anhydrous THF. Monomer 2,5,5-trimethyl-2,5-disilahepta-3,5-diyne (3 mL, 2.43 g) was added dropwise through a syringe. Following the initiation of the reaction, lots of heat was generated during the reaction. After the addition the reflux was maintained for twenty minutes. Then the reaction solvent was distilled out to afford a white solid (2.39 g). The solid had a softening point 134-136°C. The polymer was readily soluble in the common organic solvent such as THF, chloroform and toluene. The polymer had the following spectral properties. GPC: Mw=19,650, PDI=2.39. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.69 (s, 2H), 0.24 (s, 12H). ^{13}C{H} NMR ($CDCl_3$, 75.429 MHz) δ 148.73 (s, 2C), 113.23 (s, 2C), -1.67 (s, 4C). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ -31.3 ppm.

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PART TWO

POLYMERIZATION OF DIORGANODIETHYNYLSILANES: FROM POLY(SILDIACETYLENE) TO POLY(METHYLENE SILACYCLOBUTENE)

INTRODUCTION

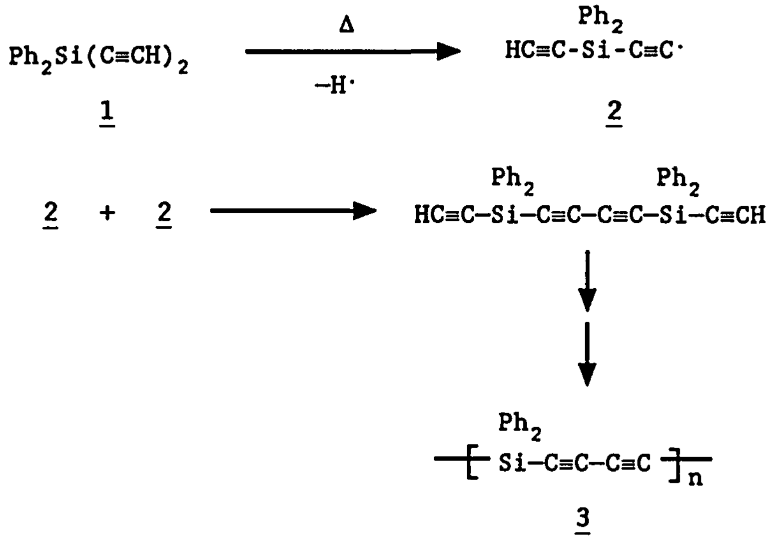
Interest in polymers with conjugated π-electron backbones[1] has grown tremendously in recent years, primarily because of its unusual electronic properties such as low energy optical transitions, low ionization potentials and high electron affinities. A major goal of the research on conducting polymers has been the development of a rechargeable plastic battery with a feature of light weight. Cells based on polypyrrole and lithium electrodes[2] have been developed in which the energy per unit mass and discharge characteristics are comparable to nickel-cadmium cells. Many other applications such as conductive polymer coatings and paints[1] are based on the fact that the electrically conductive polymers have both processing advantages of organic polymers and the electrical properties of the metals or semiconductors.

In addition to conducting electricity, the long conjugated backbone can also interfere with the propagation of light through the material, thus forcing the speed of light to vary with the intensity of the light. This is a so called nonlinear optical property. This specific phenomenon makes these materials attractive to optical computing researchers because these materials can be used in devices as optical switches-the countparts of transistors. With the aid of this device, computers could operate with pure light at a speed of about 100~1000 times as fast as the computer operated with electricity.

Although many conducting polymers have been synthesized and studied, processability and stability remains to be a problem in the applications of these conducting polymers. This part of the thesis will be devoted to a discovery and synthesis of a series of novel conducting polymers with good stability, processability and excellent nonlinear optical property.

LITERATURE SURVEY

In 1968 Luneva, Sladkov, and Korshak[3] reported that heating of diphenyldiethynylsilane 1 at 150-200°C for 20 hours produced a brick-red, brittle polymeric solids of molecular weight 3,500 which softened at 160-180°C and was soluble in organic solvents like benzene and CCl_4. The polymer was characterized by IR and ESR. The existence of high degree of electron delocalization in the polymer was suggested by a sharp narrow signal and the absence of a superfine structure in the ESR spectrum. Based on the observed hydrogen gas evolved from the polymerization, the polymer structure was assumed to be 3, containing the diacetylenic group in the polymer chain. The postulated mechanism for the formation of 3 involved initial homolytic cleavage of an acetylenic C-H bond followed by radical coupling of the resulting ethynyl radicals 2 to produce the butadiyne unit.



$$\underset{\underline{1}}{Ph_2Si(C\equiv CH)_2} \xrightarrow[-H\cdot]{\Delta} \underset{\underline{2}}{HC\equiv C-\overset{Ph_2}{Si}-C\equiv C\cdot}$$

$$\underline{2} + \underline{2} \longrightarrow HC\equiv C-\overset{Ph_2}{Si}-C\equiv C-C\equiv C-\overset{Ph_2}{Si}-C\equiv CH$$

$$\downarrow\downarrow$$

$$\underset{\underline{3}}{-\!\!\left[\overset{Ph_2}{Si}-C\equiv C-C\equiv C\right]_n\!\!-}$$

In 1975 similar result was reported by Luneva et al.[4] with different substitutes. The structures of the

$$n\ R_2M(C\equiv CH)_n \xrightarrow{\Delta} -\!\!\left[M(R)_2-C\equiv C-C\equiv C\right]_n\!\!- \;+\; n\ H_2\uparrow$$

$R = -C_6H_4OCH_3,\ -C_6H_4N(CH_3)_2,\ -C_6F_5,\ -CH{=}CH_2.$

$M = Si,\ Ge.$

polymers were studied by elemental analysis, IR and NMR spectroscopy although no detailed NMR data of the polymer were reported in that paper. Semiconductor properties of these polymers were observed and explained as a result of Pπ-dπ conjugation in the chain. The d.c. conductivity[5] at 300°K varied from 3.2×10^{-18} to 10^{-11} s/cm.

The proposed mechanism for the thermal polymerization of diphenyldiethynylsilane $\underline{1}$ is clearly incorrect since the bond dissociation energy for acetylenic C-H bond[6] is about 125±5 Kcal/mol which is much stronger than other single bonds (103 Kcal/mol for phenyl C-H bond[7], and ca. 90 Kcal/mol for Si-C bond[8]) which are present in the monomer. The homolysis of the acetylenic C-H bond is thus unlikely to take place at the reported temperature. Originating from our general interest in polymers containing alternating silicon and unsaturated carbons[9], a reinvestigation of the thermal polymerization of $(Ph)_2Si(C{\equiv}CH)_2$ $\underline{1}$ was performed.

RESULTS AND DISCUSSION

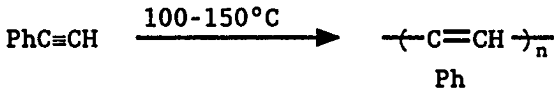
Thermal Polymerization of $(Ph)_2Si(C\equiv CH)_2$

Heating neat diethynyldiphenylsilane 1 at 150°C for 18 hours gradually produced a deep red color. The volatile material produced during heating was analyzed by an on-line mass spectrometer and found to consist solely of acetylene-no hydrogen was detected.

$$\underset{\underline{1}}{Ph_2Si(C\equiv CH)_2} \xrightarrow[\text{-HC}\equiv\text{CH (not } H_2)]{150\text{-}200°C} \underset{\underline{4}}{\text{Red Polymer}}$$

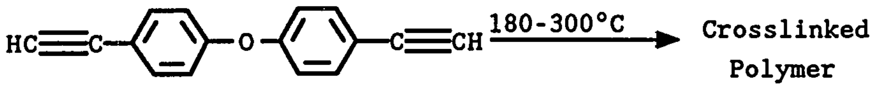
The thermal polymerization of 1 was also carried out in xylene and in diphenylether. Polymer of Mw=10,000 was obtained in this case. However in presence of hexachloroethane, Cl_3CCl_3, the polymerization was completely stopped (98% recovery of unreacted 1). Since alkylchlorides are excellent silyl radical traps[10], this result strongly indicates that the thermal polymerization is a radical process, and probably proceeds by initial homolysis of a Si-C bond to produce the initiating radicals.

It has been reported that alkynes such as phenylacetylene[11] and 4,4'-diethynylphenyl ether[12] can be thermally polymerized although the molecular weight of poly(phenylacetylene) 5 is low. During the thermal



$$PhC{\equiv}CH \xrightarrow{100\text{-}150^{\circ}C} \underset{Ph}{-(C{=}CH)_n-}$$

5, Mw=700



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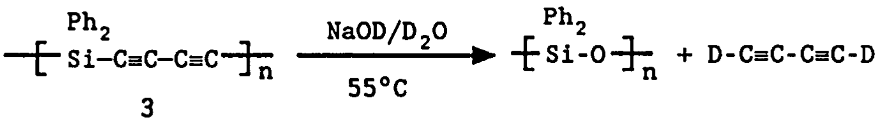
polymerization of diethynyl compounds, relatively little work[12,13] has been done regarding the chemical structure of the product. The thermal reaction of the acetylenic group is believed to be very complex. Except the conjugated polyenes, many other structural units are possible components in the product: trisubstituted benzenes from the trimerization, diacetylenic unit (-C≡C-C≡C-) from Glaser coupling, and enyne unit (-CH=CH-C≡C-) from Straus coupling.

In order to determine if the red polymer from 1 contained the silylbutadiyne units of structure 3, the red polymer 4 was decomposed by heating its solution in xylene with ca.10% NaOD in D_2O. If the structure 3 is



$$-[\overset{Ph_2}{Si}-C{\equiv}C-C{\equiv}C]_n- \xrightarrow[55^{\circ}C]{NaOD/D_2O} -[\overset{Ph_2}{Si}-O]_n- + D-C{\equiv}C-C{\equiv}C-D$$

3

correct for the red polymer 4, deuterated butadiyne should be liberated under the basic reaction condition since the silylacetylenes are extremely susceptible to cleavage by nucleophilic attack on silicon[14]. Analysis of the resulting volatile compounds by an on-line GCMS indicated ca. 1% $DC{\equiv}CD$ (mole percentage of acetylene in the diethynyldiphenylsilane). No trace of butadiyne was detected. To ascertain whether butadiyne could travel through the GC column used in our experiment, bis(trimethylsilylbutadiyne) was decomposed under the same conditions and was found to elute freely through the GC column. This result strongly suggested that there was no butadiyne unit in the red polymer <u>4</u>.

Spectroscopic analysis of the red polymer by ^{1}H and ^{13}C NMR did not supply much information due to masking by

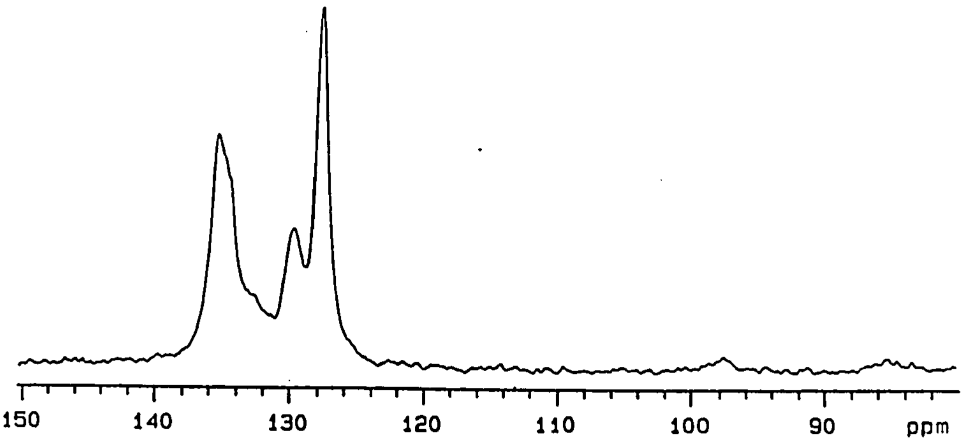


Figure 1. ^{13}C NMR spectrum of the red polymer <u>4</u>

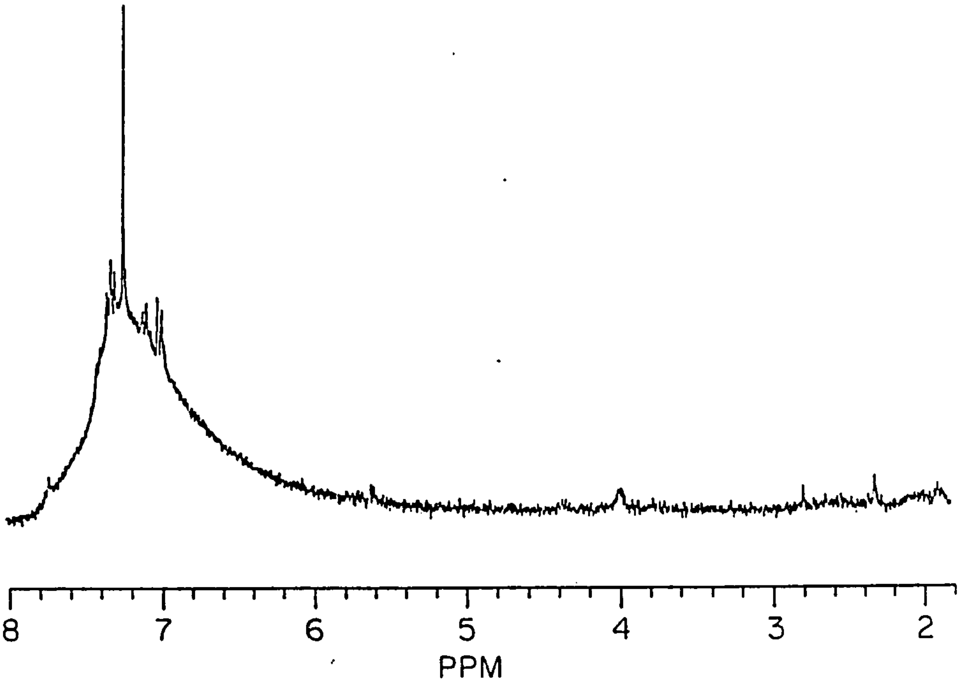


Figure 2. ^{1}H NMR spectrum of the red polymer 4

the predominant aromatic hydrogens and carbons of the phenyl substituents (Figures 1 and 2).

Weak absorptions in ^{13}C NMR at 85 ppm and 98 ppm can be attributed to unreacted acetylene which are also observed in the IR spectrum (ν C≡CH, 3,267 and 2035 cm^{-1}). ^{29}Si NMR spectra, obtained both in solid and liquid state (Figures 3 and 4), revealed silicon nuclei in a wide variety of magnetic environments, thus the red polymer 4 does not have a simple regular structure.

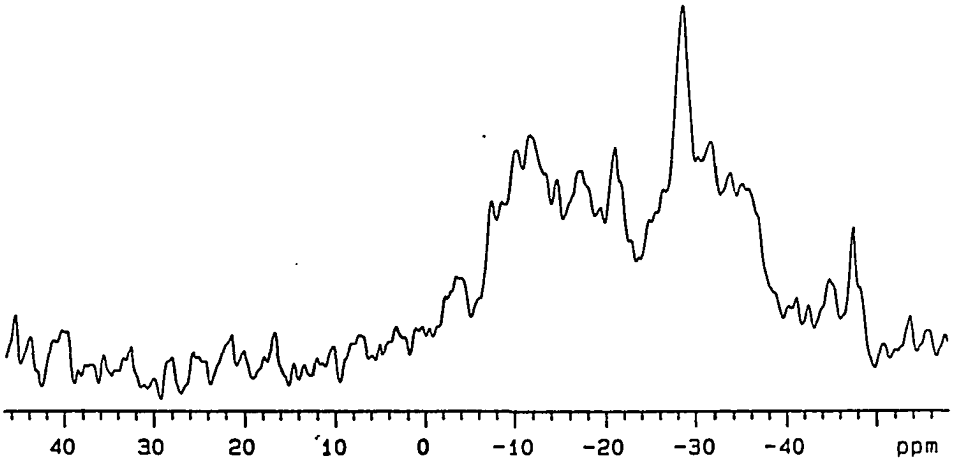


Figure 3. Liquid state ^{29}Si NMR of the red polymer 4

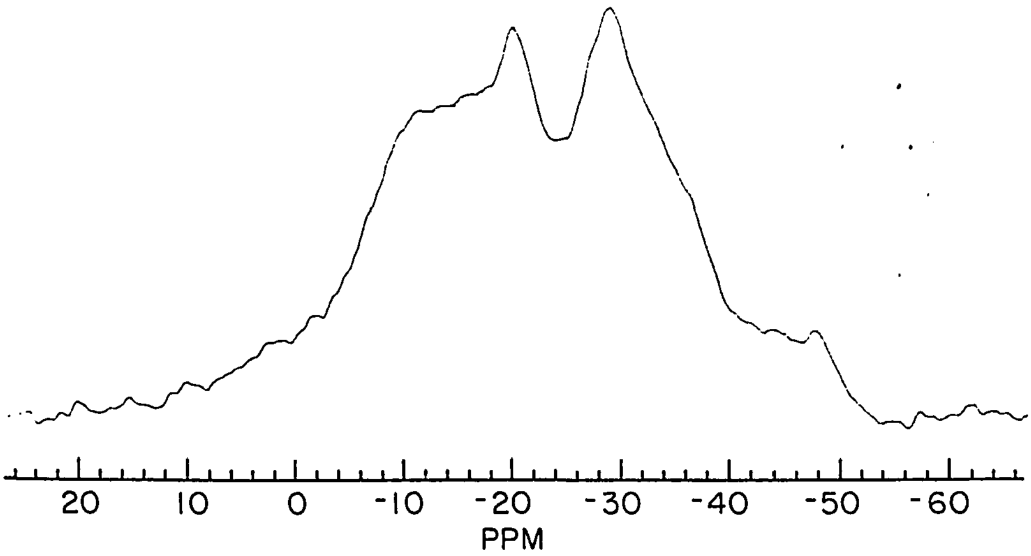


Figure 4. CPMAS ^{29}Si NMR spectrum of the red polymer 4

The ^{13}C NMR spectrum of the red polymer 4 (Figure 1) was acquired under quantitative condition by setting enough delay time. Integration of vinyl plus phenyl region (number of carbons with sp^2 hybridization, C_{sp2}) and acetylenic region (number of carbons with sp hybridization, C_{sp}) allows us to extrapolate the percentage of conversion of triple bonds into double bonds. By integration we have 140 (expressed in relative area) for sp^2 carbons (C_{sp2}) and 4.5 for sp carbons (C_{sp}). Percentage of carbon with sp hybridization ($C_{sp}\%$) is

$$C_{sp}\ \% = \frac{C_{sp}}{C_{sp2} + C_{sp}} = \frac{4.5}{140 + 4.5} = 3.1\%$$

For monomer $Ph_2Si(C{\equiv}CH)_2$

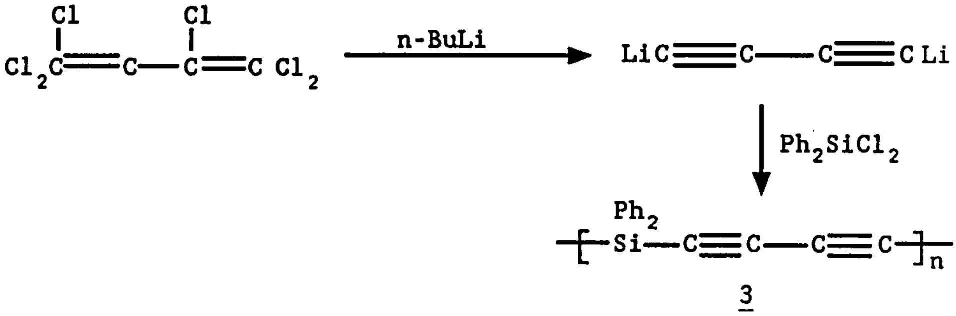
$$(C_{sp}\ \%)_{monomer} = \frac{C_{sp}}{C_{sp2} + C_{sp}} = \frac{4}{12 + 4} = 25\%$$

For the polymer, suppose that x% of C≡C has been transformed into C=C. Then (1-x%) is the percentage of C≡C left in the polymer, and 4(1-x%) is the number of C≡C in the polymer while ($C_{sp2} + C_{sp}$) remains to be (12 + 4). Correlating this result with the experimental value, equation (1) is obtained. Solving the equation (1) for

$$\frac{4\ (1 - x\%)}{12 + 4} = 3.1\% \qquad (1)$$

x%, we have x%=87.6%. So about 87.6% of acetylene is transformed into double bond in the thermal polymerization.

The most conclusive evidence for the elimination of 3 as the structure of the red polymer 4 came from an independent synthesis of 3[15]. Treatment of hexachlorobutadiene with four equivalents of n-butyllithium in THF at -78°C followed by quenching with diphenyldichlorosilane afforded polymer 3 as a light yellow solid (Mw = 10,000). The polymer 3 was characterized by ^{13}C NMR (Figure 5, acetylenic carbons



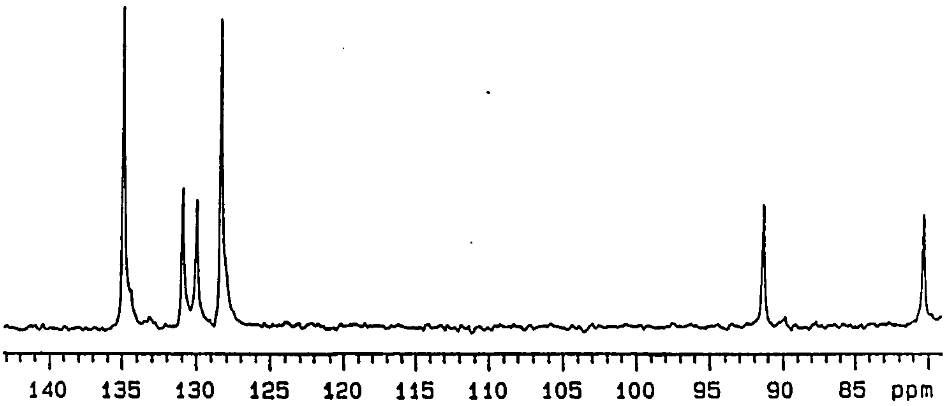


Figure 5. ^{13}C NMR spectrum of polymer 3

at δ 80 and 91 ppm) and ^{29}Si NMR (single sharp peak at δ -47 ppm). Thus it is conclusively established that the thermal polymerization of $Ph_2Si(C{\equiv}CH)_2$ does not produce poly(diphenylsildiacetylene) 3.

In order to further prove the assumption that the triple bonds in diphenyldiethynylsilane were transformed to double bonds during the thermal polymerization, dimethyldiethynylsilane was also synthesized. Heating of

$$HC{\equiv}CMgCl + Me_2SiCl_2 \xrightarrow{THF}$$

$$\underset{\underline{8}\ (97\%)}{Me_2Si(C{\equiv}CH)_2} + \underset{\underline{9}\ (2\%)}{HC{\equiv}C\text{-}SiMe_2\text{-}C{\equiv}C\text{-}SiMe_2\text{-}C{\equiv}CH}$$

$$\underline{8} \xrightarrow{150\text{-}200°C} \text{Dark Red Solid } \underline{10}$$

$$\underline{9} \xrightarrow{150\text{-}200°C} \text{Dark Red Solid } \underline{11}$$

dimethyldiethynylsilane 8 or trialkyne 9 under the same condition as employed for diphenyldiethynylsilane produced an intractable, dark red solid in both cases. Spectroscopic analysis of the red polymer 10 by solid state ^{29}Si NMR (Figure 6) revealed that thermal polymerization of 8 had similar feature as in red polymer 4 based on the broad resonance absorption. Solid state ^{13}C NMR of the red polymer 10 (Figure 7) clearly indicated that most triple bonds were transformed into double bonds during the heating.

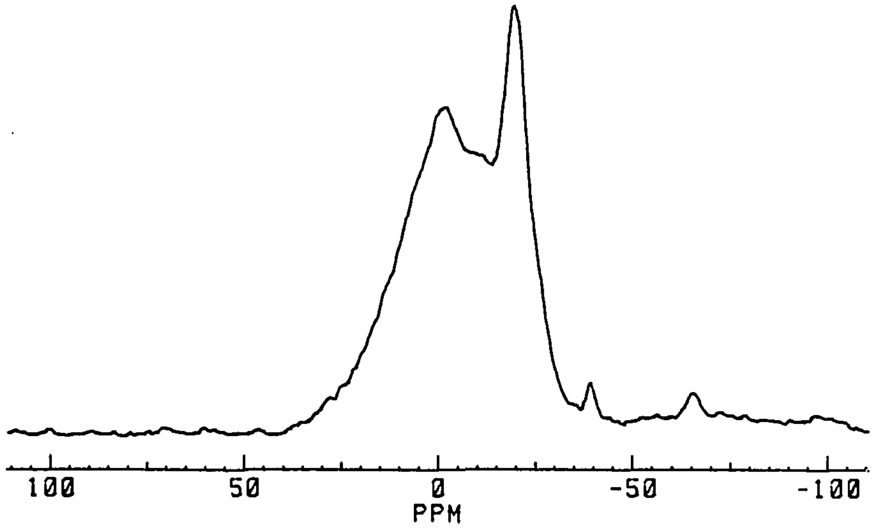


Figure 6. CPMAS ^{29}Si NMR spectrum of the red polymer 10

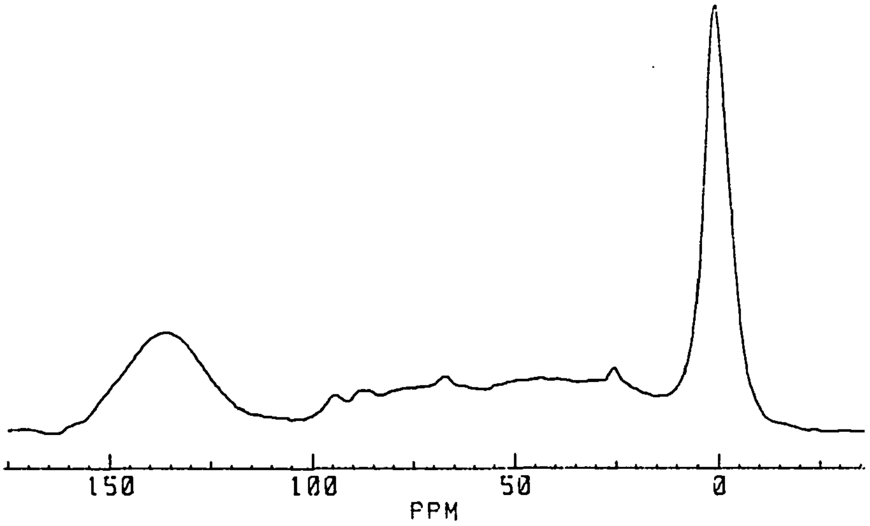


Figure 7. CPMAS ^{13}C NMR spectrum of the red polymer 10

In Figure 7 the broad resonance signals between 120-170 ppm is due to the vinyl carbons formed during the thermal polymerization. Two minor peaks at ca. 85 and 95 ppm are coming from the unreacted acetylene. Solid state ^{13}C NMR spectrum of the red solid 11 is shown in Figure 8. It is interesting to notice that not only the terminal acetylenes in the dimer 9 but also the internal disubstituted acetylene can be transformed into the double bonds under the condition used.

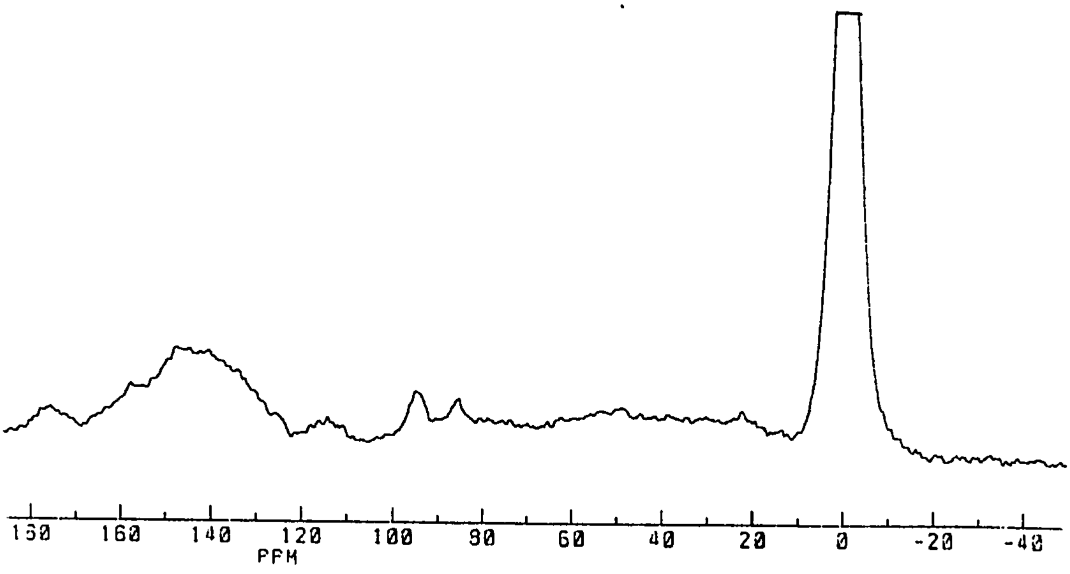


Figure 8. CPMAS ^{13}C NMR spectrum of the red polymer 11

Deuterated compound <u>12</u> was also synthesized and was thermally polymerized in order to observe the vinyl deuterium by ^2H NMR. The observed ^2H NMR spectrum was a

$$Ph_2Si(C{\equiv}CH)_2 + 2\ MeMgCl_2 \xrightarrow{THF} \underset{\underline{12}}{Ph_2Si(C{\equiv}CMgCl)_2}$$

$$\underline{12} + DCl/D_2O \longrightarrow \underset{\underline{13}}{Ph_2Si(C{\equiv}CD)_2}$$

$$Ph_2Si(C{\equiv}CD)_2 \xrightarrow{150\text{-}200°C} \underset{\underline{14}}{\text{Red Polymer}}$$

bimodel broad signal which covered from -1 ppm to 11 ppm (with one broad peak centered at 6.5 ppm and the other at ca. 2.5 ppm in about equal intensity). The reason why ^2H NMR resonance signal was so broad was not clear. In order to prove that the unusually broad resonance signal in ^2H NMR was not due to a strange behavior of the quadrupole nuclei (spin of $^2H = 1$) and in a continuous effort to quantitatively characterize the ratio of the vinyl protons to acetylenic protons, phenyl deuterated compound <u>16</u> was synthesized. Thermal polymerization of compound <u>16</u> under the same condition as before afforded a red solid.

The ^1H NMR of the red polymer <u>17</u> (Figure 9) was

$$C_6D_5Br + Mg \xrightarrow{\text{ether}} C_6D_5MgBr$$

$$C_6D_5MgBr + SiCl_4 \longrightarrow (C_6D_5)_2SiCl_2 \quad \underline{15}$$

$$\Big\downarrow \text{2 HC}\equiv\text{CMgCl}$$

$$(C_6D_5)_2Si(C\equiv CH)_2$$

$$\underline{16} \text{ (77\% overall)}$$

$$(C_6D_5)_2Si(C\equiv CH)_2 \xrightarrow{150\text{-}200^\circ C} \text{Red Polymer } \underline{17}$$

still featured with a broad bimodal resonance signal which covered a range from 0 ppm to 9 ppm. In Figure 9 the sharp resonance at ca. 0 ppm is due to the TMS added in the solution, sharp resonance at ca. 5.3 ppm is coming

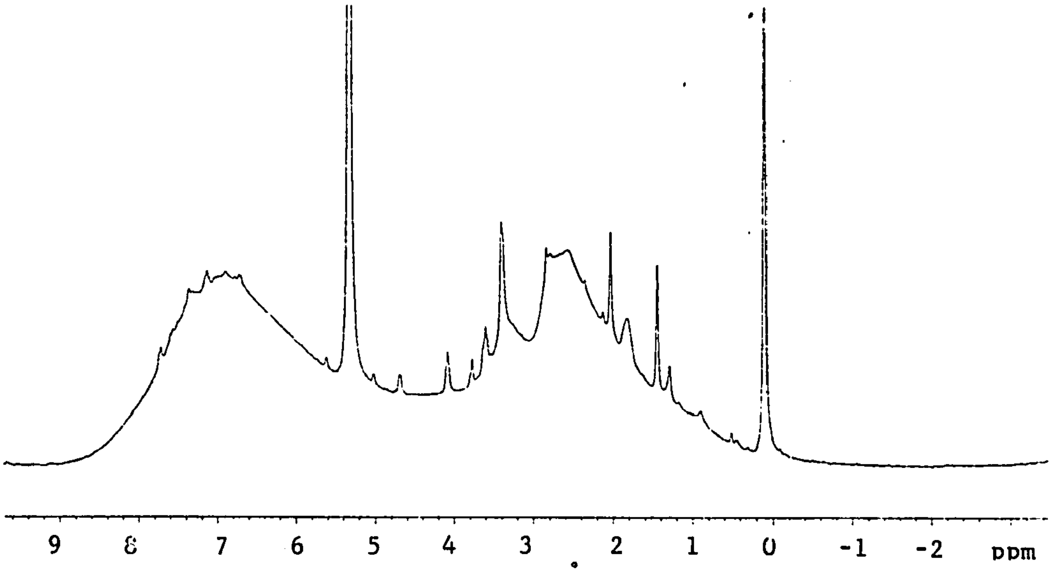
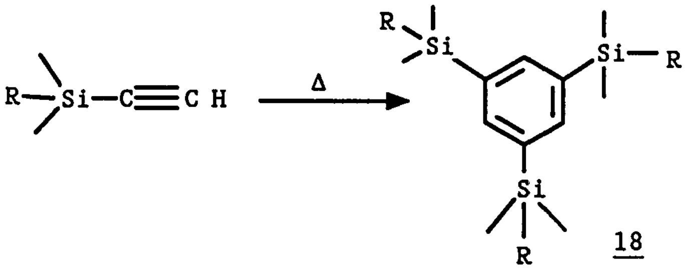


Figure 9. ^{1}H NMR spectrum of red polymer 17

from the solvent methylene chloride. Of the two broad signals, one centered at ca.7 ppm is assigned to vinyl proton and the other centered at 2.6 ppm is acetylenic proton. If these assignments are correct, it seems that only about half of the triple bonds were transformed into double bonds during the thermal polymerization. The broad resonance of the vinyl proton again revealed that the vinyl proton in the red polymer had a wide variety of magnetic environments, so the chemical structure of the red polymer is not regular and must be complicated.

The possibility of symmetry-allowed [2+2+2] cyclotrimerization of the acetylene during heating of $Ph_2Si(C\equiv CH)_2$ was eliminated by a bromination experiment on the red polymer. In [2+2+2] cyclotrimerization of the acetylenes, substituted benzene 18 would be formed. It



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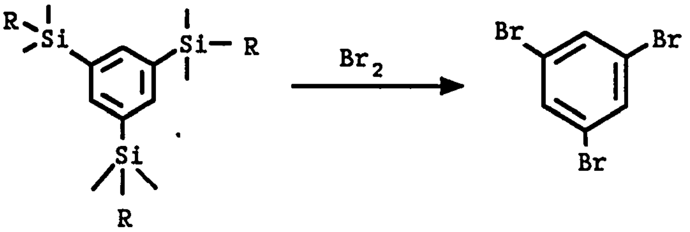
has been reported that the Si-Ph bond could be quantitatively cleaved by bromination[16] in chloroform at elevated temperature. Thus treatment of compound 18 with bromine should quantitatively produce tribromo- benzene.

Thus the red polymer 4 was refluxed with excess bromine

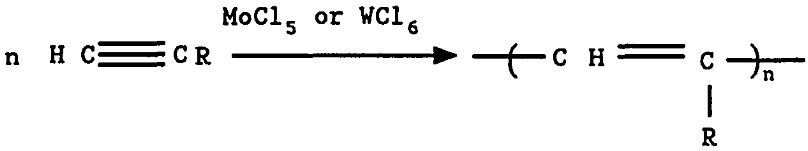


in chloroform, mono-bromobenzene was produced but no dibromo- or tribromo-benzene was observed based on the GC-MS analysis of the product. Authentic 1,3,5-tribromobenzene was injected into the same GC-MS to assure that di- and tri-bromobenzene (if generated from the red polymer) could travel through the column and be detected.

From the combination of the NMR spectroscopic results and the bromination results, it is clear that during the thermal polymerization of diphenyldiethynylsilane the triple bonds were transformed into double bonds to form a polyacetylene type structure in the red polymer 4.

Catalytic Polymerization of $Ph_2Si(C{\equiv}CH)_2$

Recently Masuda and Higashimura[17] reported that substituted acetylenes could be polymerized in the presence of Mo and W catalysts to give polyacetylenes with high molecular weights.



$$n\ HC{\equiv}CR \xrightarrow{MoCl_5\ \text{or}\ WCl_6} -\!\!(CH{=}\underset{R}{\underset{|}{C}})_n\!-$$

Catalysts $Mo(CO)_6$-CCl_4-$h\nu$, $MoCl_5$ and WCl_6 have been used in the polymerization of $Ph_2Si(C{\equiv}CH)_2$. The experimental results are summarized in Table 1. In striking contrast to thermal polymerization, polymerization by using catalysts $MoCl_5$ and WCl_6 affords a deep violet material with vastly improved molecular weight.

$$Ph_2Si(C{\equiv}CH)_2 \xrightarrow{\text{Mo or W Cat.}} \text{Violet polymer}$$

19

Table 1. Catalytic polymerization of diphenyldiethynylsilane

monomer	catalyst	temp(°C)	solvent	color	Mw
1	$Mo(CO)_6$-$h\nu$	80	CCl_4	red	10,000
1	$MoCl_5$	60	benzene	violet	105,308
$Ph_2Si(C{\equiv}CD)_2$	$MoCl_5$	60	benzene	violet	100,000
1	WCl_6	25	toluene	violet	34,000

The UV spectra of 19 (Figure 10) is strikingly different from that of thermally polymerized red polymer 4 with the λ_{max} of ca. 540 nm which indicates an extensive conjugation and a relatively defined electronic structure existing in the polymer. This is consistent with the observed ^{29}Si NMR spectrum (Figure 11) of violet polymer where the intensity of the resonance signal at δ -21 ppm is dramatically increased. These results reveal that the regular structure in the polymer is greatly increased when the catalysts are used. ^{1}H NMR and ^{13}C NMR (Figure 13) spectra of violet polymer <u>19</u> are similar to those of red polymer <u>4</u> and are thus relatively uninformative due to the predominant absorption from the phenyl groups.

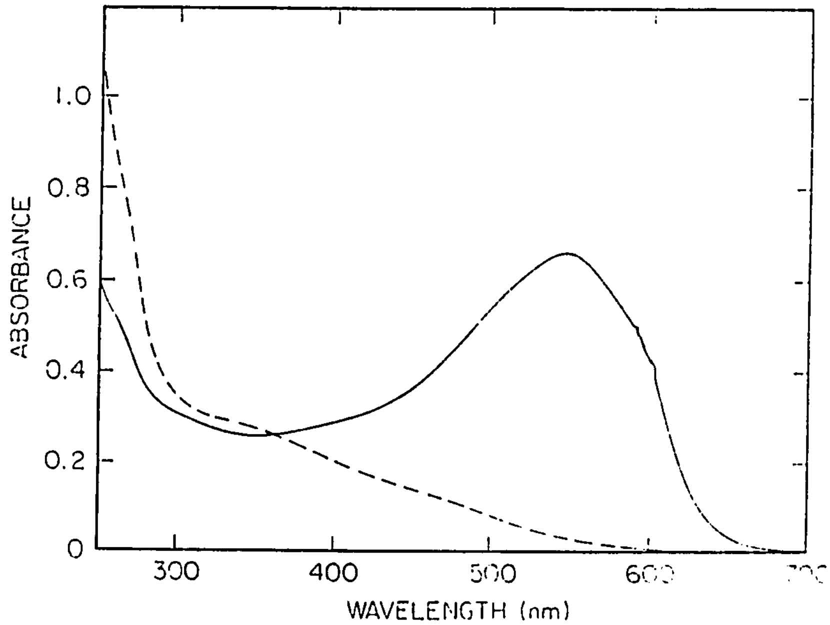


Figure 10. UV-visible spectra of red polymer <u>4</u> (dashed line) and violet polymer <u>19</u> (solid line)

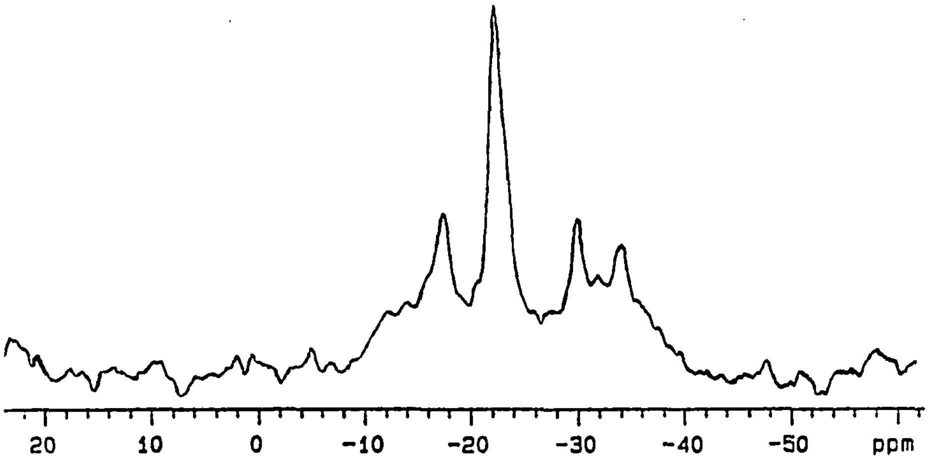


Figure 11. Liquid state ^{29}Si NMR of violet polymer 19 with catalyst $MoCl_5$

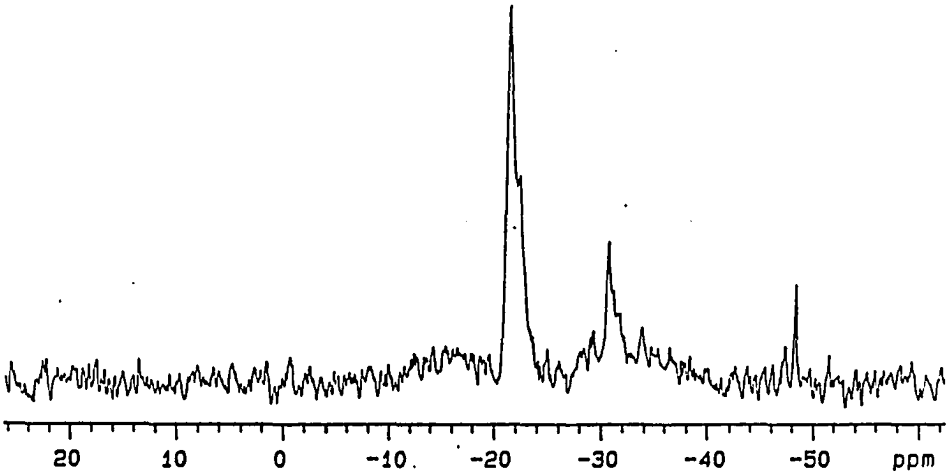


Figure 12. Liquid state ^{29}Si NMR of violet polymer 19 with catalyst WCl_6

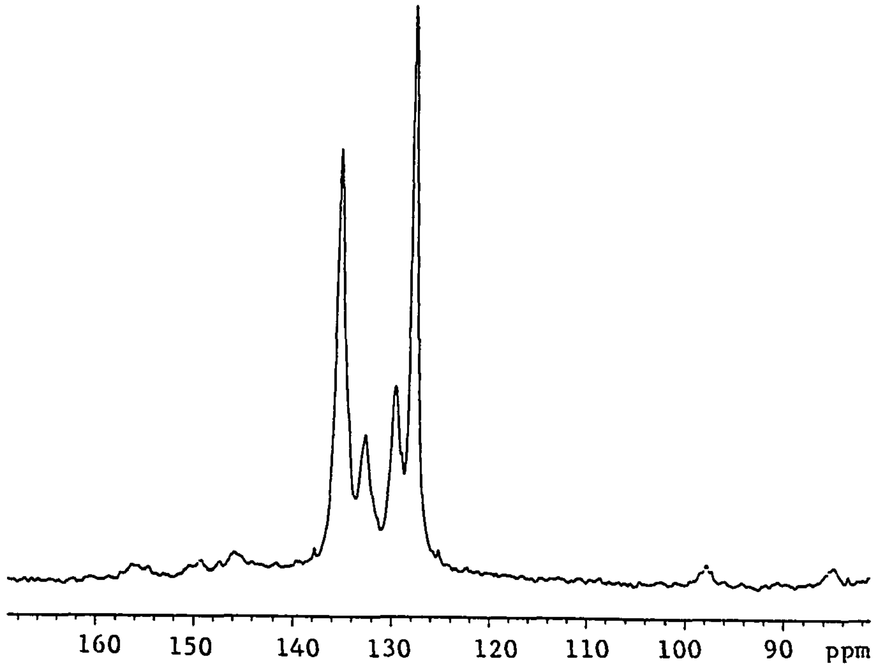


Figure 13. Liquid state ^{13}C NMR of violet polymer <u>19</u> with catalyst WCl_6. Resonance signals at ca. 85 ppm and 98 ppm are due to residue acetylene groups. Broad signals from 140 to 158 ppm are corresponding to the chemical structure in the polymer chains

Because of the dominating phenyl protons and carbons, ^{1}H and ^{13}C nuclei turn to be of little help in the further characterization of the violet polymer 19. Fortunately relative sharp resonance signals in ^{29}Si NMR are present for the polymers resulting from the catalytic polymerization, which can be used to extract more structural informations. The resonance absorption range can be divided into three regions: a broad resonance from -10 to -20 ppm, a relative sharp resonance signal from -20 to -26 ppm, and another broad peak from -26 to -42 ppm. The ^{29}Si NMR spectra were acquired under quantitative conditions by using a 90 degree pulse and a proton gated decoupling sequence with enough length of time delay. The integral intensities and UV-visible absorptions are summarized in Table 2. If the sharp signal occurring between -20 to -26 ppm corresponds to a regular structural unit in the polymer, then the content of this unit basically remains the same (within experimental error) when the catalyst was changed from $MoCl_5$ to WCl_6. When lower temperature and lower concentration of the monomer were used, however, the content of the regular structural unit was significantly increased. Regarding to the solubility and UV-visible absorption, the polymer from $MoCl_5$ had better properties.

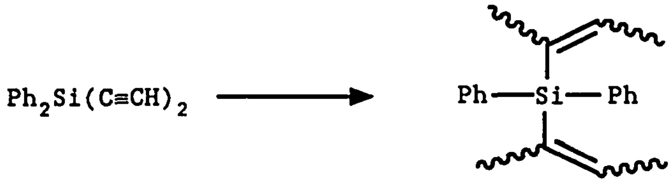
Table 2. Structural comparisons of poly(diphenyldiethynylsilane) from different catalylyst

Catalyst	Temp (°C)	Integral intensities (%)			UV-visible[a] λ_{max}	solubility
		-10 to -20 ppm	-20 to -26 ppm	-26 to -42 ppm		
$MoCl_5$	60	28.8	35.6	35.6	550 nm	good
WCl_6	60	25.8	36.2	38.0	540 nm	partially soluble
WCl_6	25[b]	18.7	47.5	33.7	480 nm	good

[a] UV spectra were taken in THF solvent.

[b] 50% lower monomer concentration was used in this case.

So far all the information has unambiguously indicated that most triple bonds in monomer $Ph_2Si(C{\equiv}CH)_2$ have been transformed into double bonds in both thermal and catalytic polymerizations. The basic unit to build the polymer backbone can be drawn as follow, i.e., unit 20.



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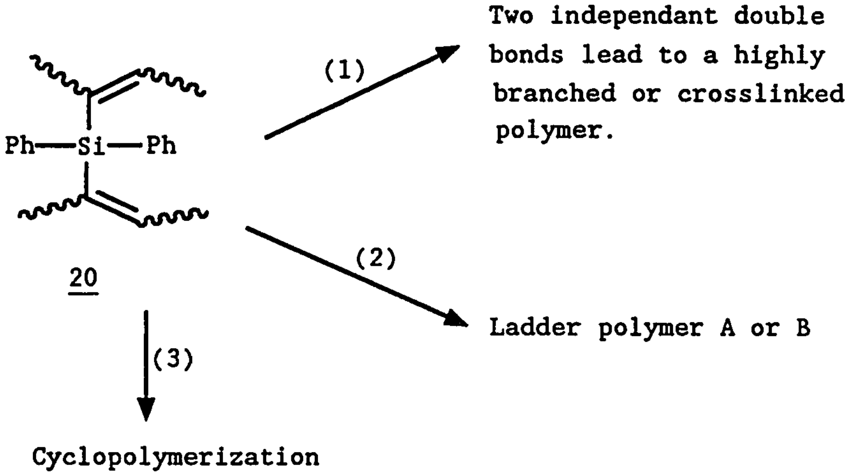
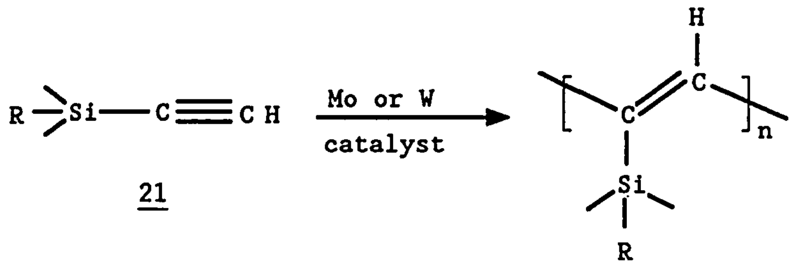
As to the chemical structure of the violet polymer 19, possible connections of the basic unit 20 to construct conjugated polymer backbones are listed as follows: (1) two double bonds in each unit 20 behave independently to form a highly branched or crosslinked net-work structure, (2) units 20 are connected side by side to form a ladder polymer with a structure A or B (shown later), and (3) two double bonds in unit 20 relate to each other to form a ring, i.e., cyclopolymerization where three-, four-, and five- membered ring are possible. Detailed considerations will be discussed in the following context.



The possibility (1) can be excluded based on the following argument. First, this structure can not explain the UV-visible absorption observed for the violet polymer. Two independent double bonds mean the two triple bonds react independently like two individual acetylenes during the polymerization. Regarding to the coplanarity between the adjacent double bonds, polyacetylene backbone formed in this case would have a similar structure as in monosubstituted acetylene. For example, silyl substituted acetylene[18] 21 can be polymerized in the presence of $MoCl_5$ or WCl_6 catalyst, where R is methyl, n-hexyl, phenyl, and phenylethyl. It is well known that substituted polyacetylenes are generally colorless or light yellow with UV λ_{max} between 260-330nm[17]. This is ascribed to the noncoplanarity of adjacent double bond repeat units, which effectively



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diminishes the overlap between p-orbitals. Increasing the content of branching or crosslinking in the polymer will further interrupt the coplanarity of the conjugated backbone. This is not in keeping with the UV spectrum observed for the violet polymer.

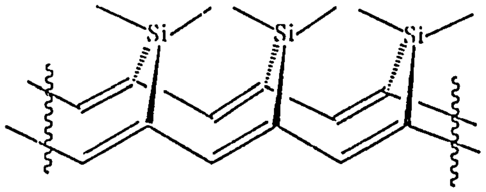
Secondly, if the two acetylene groups in the monomer behave independently, the average functionality f_{avg} for each monomer equals four. From Carothers equation[19] the critical extent of reaction P_c at the gel point can be calculated as

$$P_c = \frac{2}{f_{avg}} = \frac{2}{4} = 0.5$$

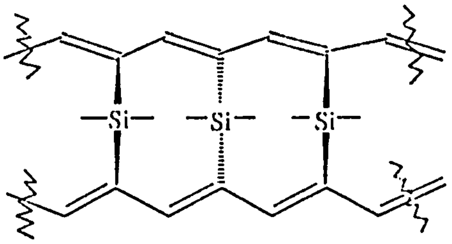
This result means that gel will be formed at 50% conversion of the triple bond. The high conversion of acetylene in the violet polymer (ca. 90% based on carbon-13 NMR) and the ready solubility of the violet polymer in common organic solvents are not consistent with the conclusion derived from Carothers equation. As a result the two acetylene groups must relate to each other during the polymerization in some way that the average functionality of the monomer is close to two since a soluble high molecular weight polymer is obtained.

A second possible structure for the polymer is a ladder polymer. There are two possible ladder conformations which will form corresponding ladder polymers A and B as shown below.

Ladder polymer A:



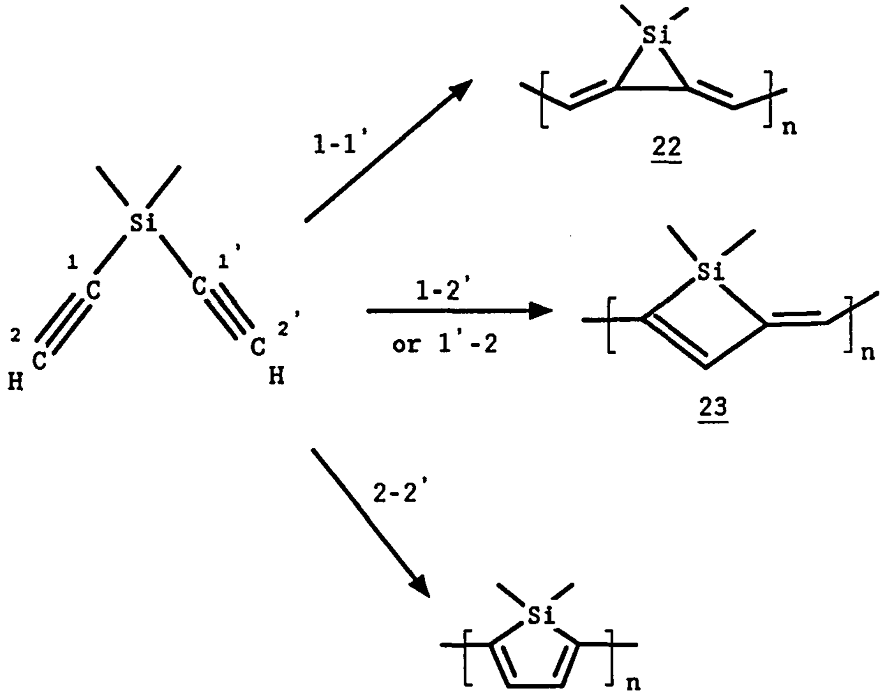
Ladder polymer B:



In both cases, substituted groups on silicon atoms are not shown. In ladder polymer A, all of the silicon atoms are located on the same side of the double-strand (or more exactly, parallel) polyacetylene backbones. Model studies of the ladder A indicate that there is no room to put any two substituents between the adjacent two silicon atoms. In another word, the ladder polymer A is very crowded and not possible to construct.

In the ladder polymer B, silicon atoms are located alternatively up and down relative to the plane which contains the two parallel polyacetylene backbones. Although steric hindrance of the substitutes on silicon atoms is released in this case, p-orbitals are twisted ca. 50 to 60 degrees away from coplanarity, i.e., π-bonds become almost orthogonal. This will completely destroy the overlap between p-orbitals, so no UV-visible absorption is expected from the ladder polymer B.

Based on the experimental evidences and the above reasonings, the two ethynyl groups in the same monomer must react with each other to form a ring structure in order to have an average functionality of about two, i.e., cyclopolymerization must occur during the polymerization of diphenyldiethynylsilane. If we label two acetylene groups in such a way that we can distinguish them, for example label one acetylene by "1" and "2" while the other by "1 prime" and "2 prime", all possible connections between two acetylenes are 1-1', 1-2'(=2-1'), and 2-2' which will lead to corresponding three-, four-, and five-membered ring.



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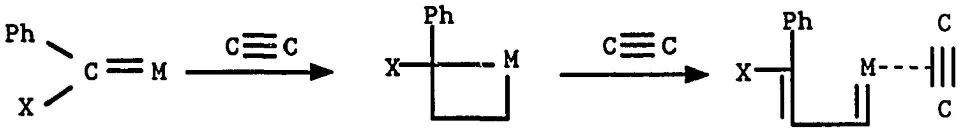
Mechanistically, all three-, four- and five-membered rings are possible to form. The initiation reaction[20] (formation of propagating species) with metal carbene catalysts 25 can be simply expressed as follow



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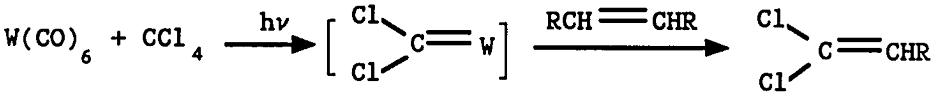
It has been confirmed by trapping experiment that tungsten dichlorocarbene 26 forms in the W(CO)$_6$-CCl$_4$-hν system[21]. In a mixture of acetylene compounds and

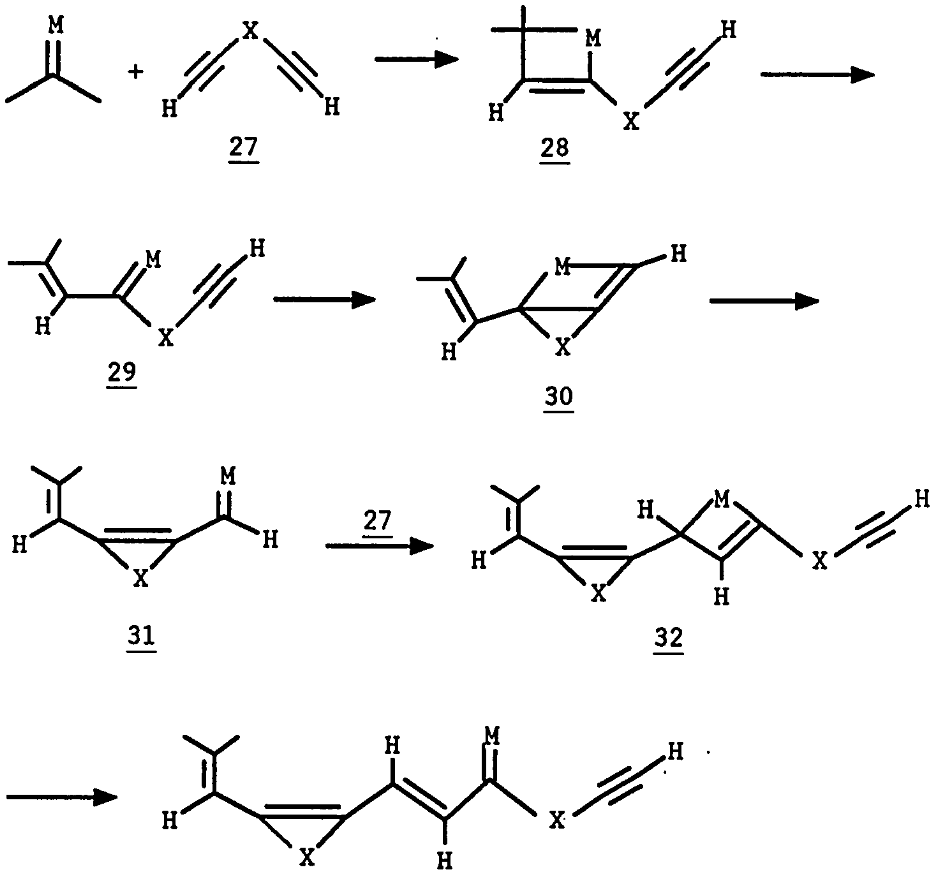


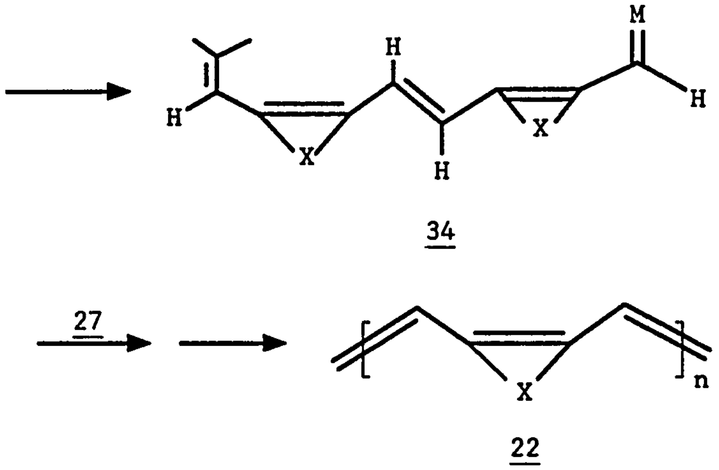
$W(CO)_6 + CCl_4 \xrightarrow{h\nu} [Cl_2C{=}W] \xrightarrow{RCH{=}CHR} Cl_2C{=}CHR$

26

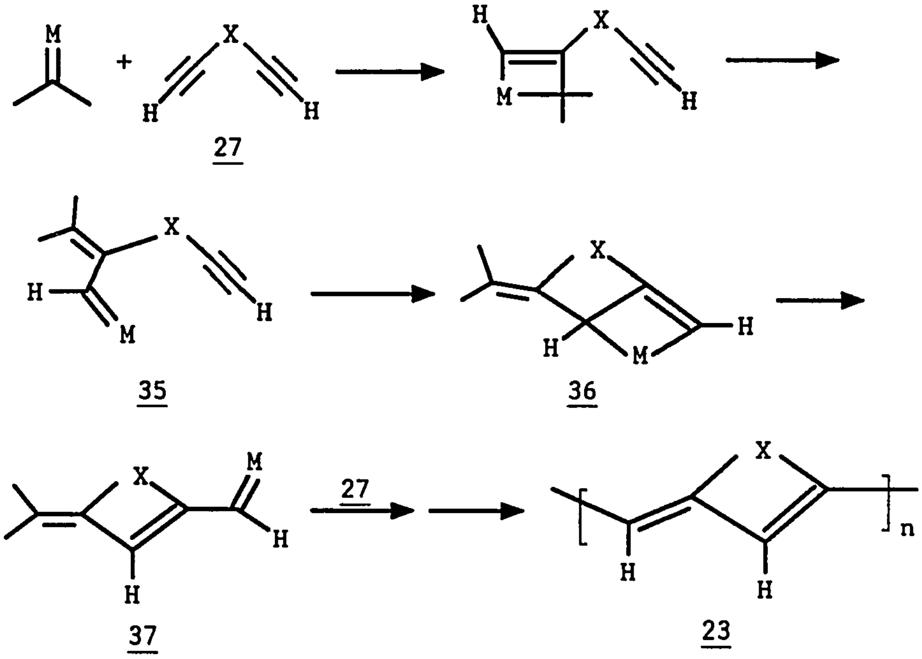
metathesis catalysts, metal carbenes are generated somehow and serve as active species in the polymerization. Proposed mechanisms for the formation of ring structures 22, 23 and 24 are listed as follows.

Mechanism for three-membered ring:

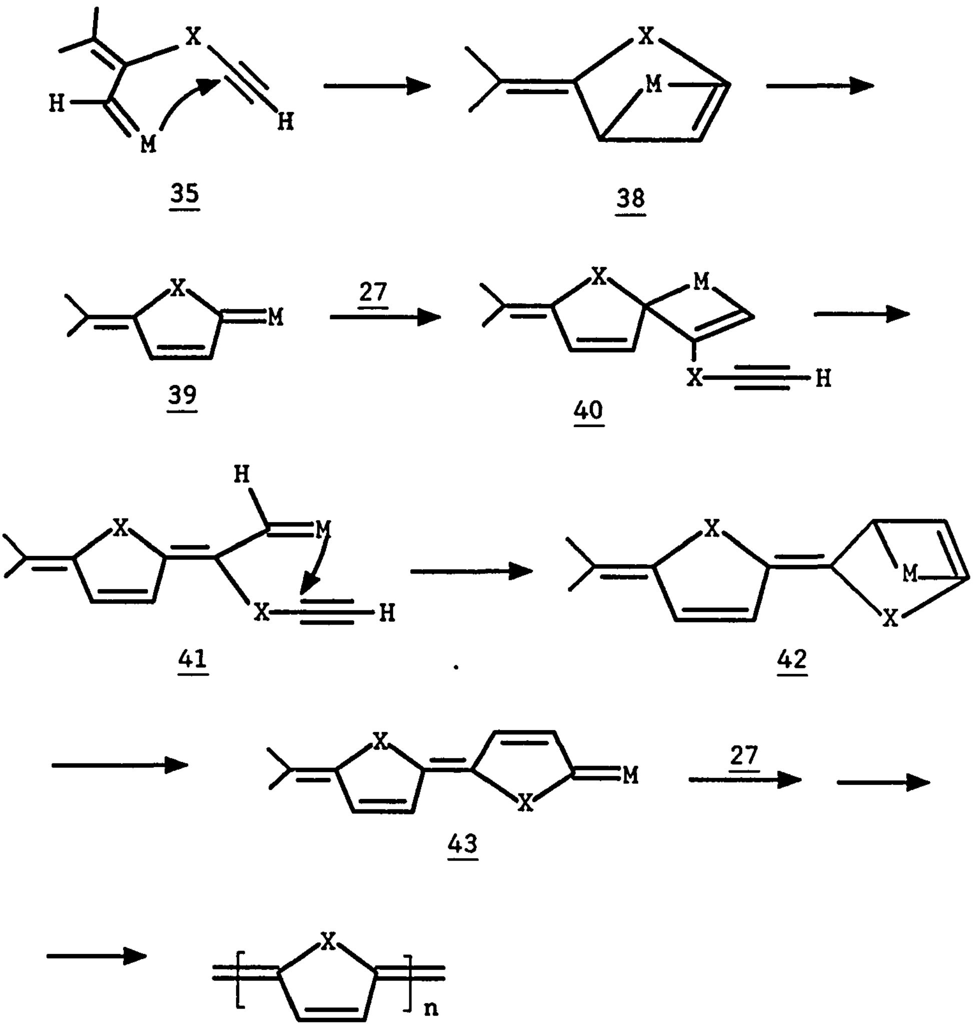




Mechanism for four-membered ring:



Mechanism for five-membered ring:



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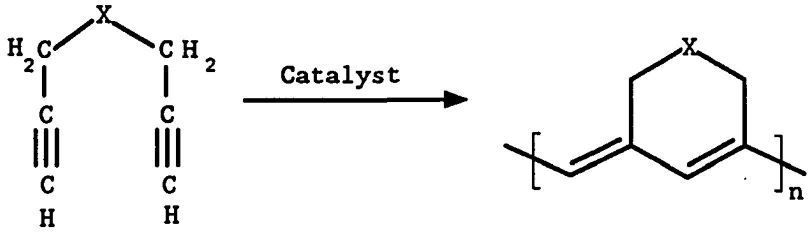
Many studies[22-25] about the cyclopolymerization of nonconjugated diynes, 1,6-heptadiyne and its analogues, have been reported recently. 1,6-Heptadiyne[22] (<u>44</u>, X = CH_2) can be polymerized in the presence of a Ziegler-Natta catalyst [$TiCl_4/Al(i\text{-}C_4H_9)_3$] to produce an insoluble polymer film with high electrical conductivity



44

45

X = CH_2, S, O, SiR_2, GeR_2

(up to 1 s/cm when doped with iodine and arsenic pentafluoride). $MoCl_5$ and WCl_6 are also effective catalysts in the polymerization of 44 (X = S, O, SiR_2 and GeR_2), however the polymers obtained in this case are generally soluble. The structure of the polymers has been tentatively assigned to be a six-membered ring 45 based on a thermal stability argument[22] although no conclusive spectroscopic evidence of structure 45 has been observed.

In the violet polymer 19, further distinction among the three-, four- and five-membered rings is obstructed by the predominant phenyl groups and the broad resonance signals in the ^1H and ^{13}C NMR spectra.

Catalytic Polymerization of Di(secondary alkyl)-diethynylsilane, $(2°\text{-}R)_2Si(C\equiv CH)_2$

In a continuous effort to characterize the structure of the violet polymer 19, and to explore the polymerization of diethynylsilane systems, (sec-Bu)$_2$Si(C≡CH)$_2$ 47 and (iso-Pr)$_2$Si(C≡CH)$_2$ 48 were synthesized. Choice of a secondary alkyl group is based on the similarity of steric hindrance to the phenyl group.

$$\mathrm{RLi} + \mathrm{SiCl_4} \xrightarrow{\text{hexane}} \underset{\underline{46}}{\mathrm{R_2SiCl_2}}$$

$$\mathrm{R_2SiCl_2} + 2\ \mathrm{HC{\equiv}CMgCl} \xrightarrow{\text{THF}} \mathrm{R_2Si(C{\equiv}CH)_2}$$

$\underline{47}$, R = Sec-Bu

$\underline{48}$, R = iso-Pr

Both monomers 47 and 48 were characterized by ^{1}H, ^{13}C and ^{29}Si NMR. For (iso-Pr)$_2$Si(C≡CH)$_2$, a single ^{29}Si resonance at -23 ppm and four ^{13}C signals (95.3, 82.9, 17.1 and 11.6 ppm) in the proton-decoupled spectra were observed. In the case of (sec-Bu)$_2$Si(C≡CH)$_2$, however, complicated spectra in ^{1}H, ^{13}C and ^{29}Si NMR were exhibited. ^{1}H NMR spectrum (Figure 14) shows a triplet at 1.00 ppm and a doublet at 1.09 ppm for two methyl groups respectively, a triplet at 2.45 ppm for the acetylenic proton. A complex three spin (AMX) system, however, is observed for methylene and methine protons! These three protons in the AMX system are strongly coupled each other as further proved by a 2D COSY spectrum displayed as a contour plot in Figure 15.

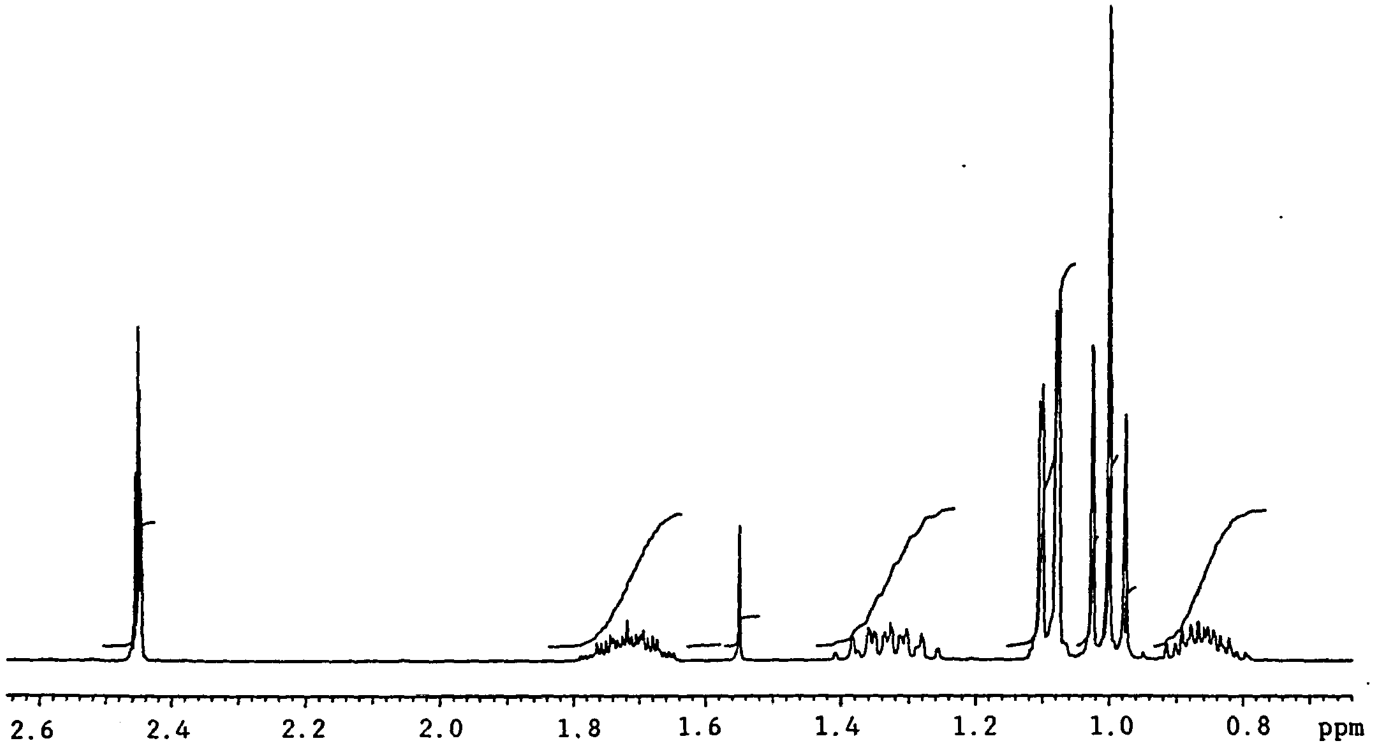


Figure 14. ^{1}H NMR spectrum of di(sec-butyl)diethynylsilane

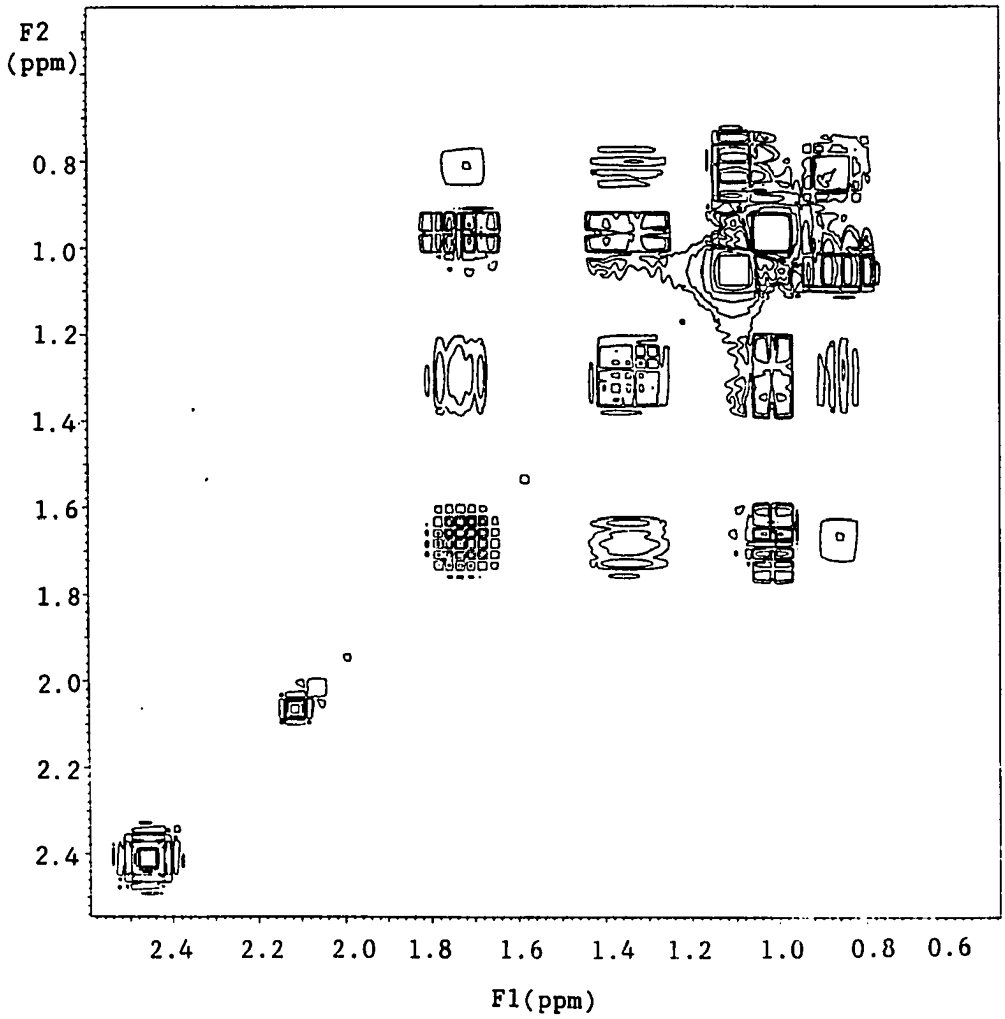


Figure 15. ^{1}H COSY spectrum (contour plot) of di(sec-butyl)diethynylsilane. Off-axis peaks are indicative of homonuclear spin-spin coupling

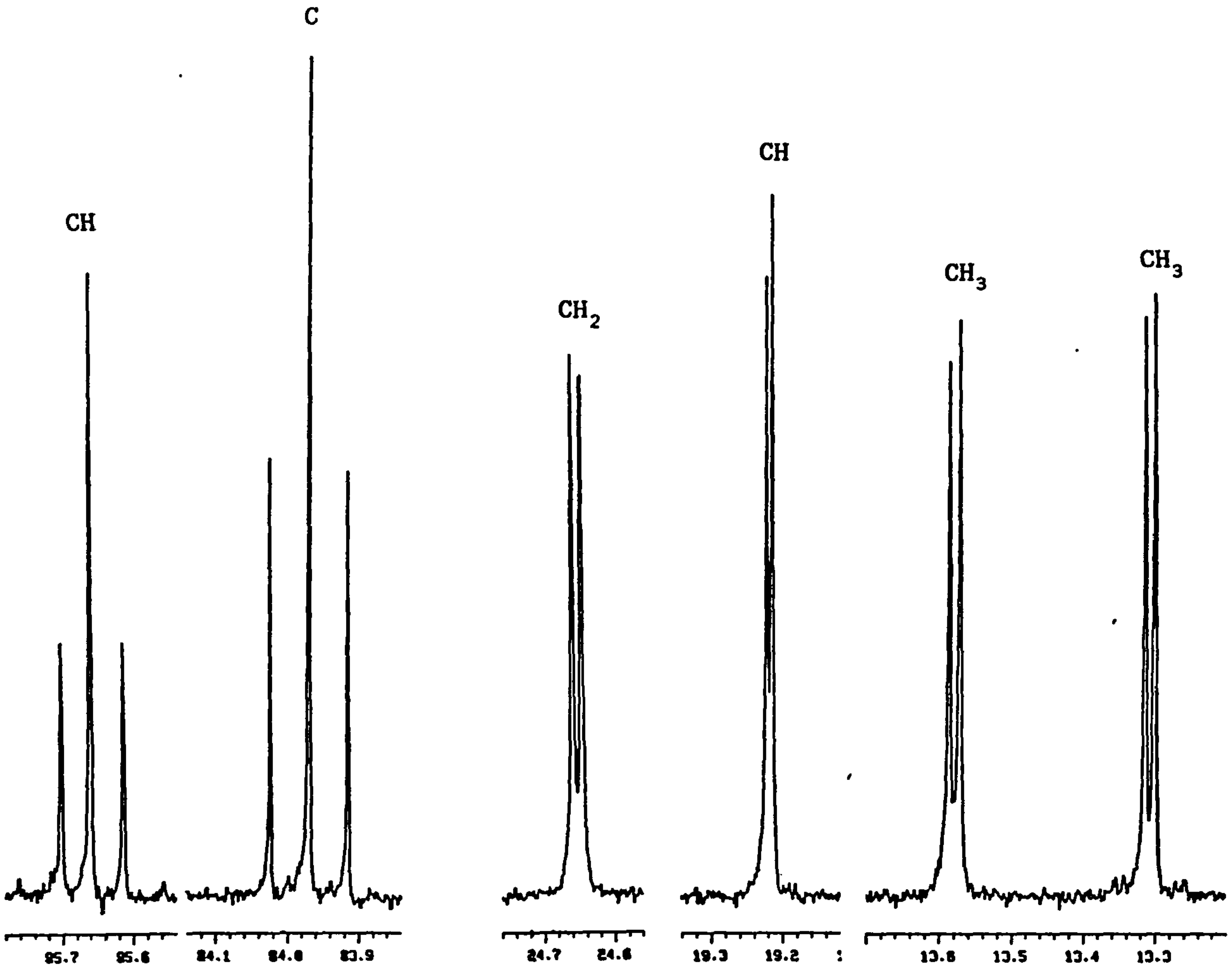


Figure 16. Quantitative ^{13}C NMR spectrum of (sec-Bu)$_2$Si(C≡CH)$_2$ with ^{1}H-gated decoupling

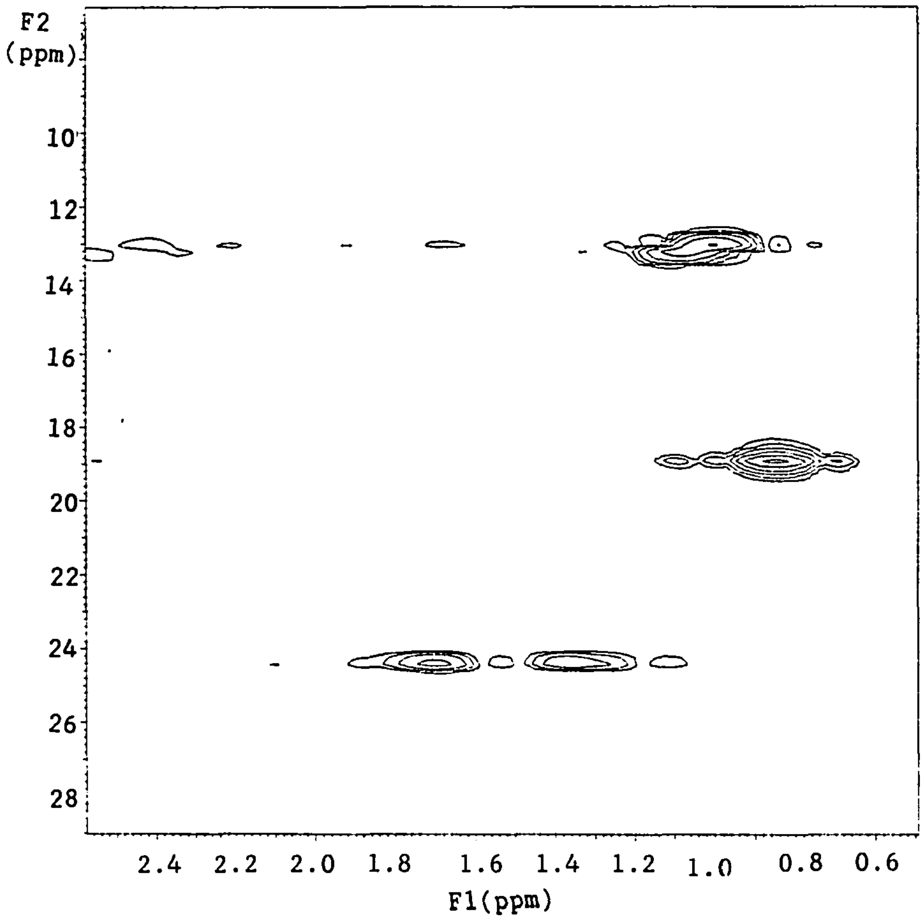
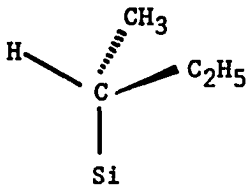


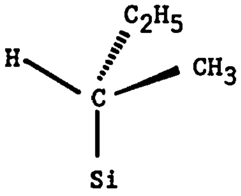
Figure 17. ^{13}C / ^{1}H two dimensional correlated spectrum of di(sec-butyl)diethynylsilane in a contour plot

With the aid of a proton-carbon heteronuclear shift correlation experiment (Figure 17), resonance at ca. 0.86 ppm is assigned to the methine proton, while resonances at ca. 1.32 and 1.72 ppm belong to the methylene protons. In ^{13}C NMR (Figure 16), a doublet for each carbon on sec-butyl substitute, a triplet for each ethynyl carbon were observed. In ^{29}Si NMR, a doublet resonance signals of -25.527 ppm and -25.580 ppm were exhibited.

The above misleading spectra for $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$ can be explained when the stereogenic center on two sec-butyl substitutes is considered. Each sec-butyl substitute can take either S- or R-configuration as shown below:

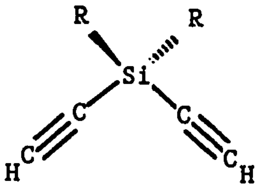


(R)-Configuration

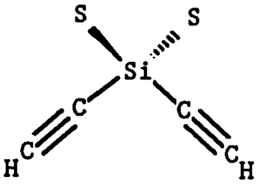


(S)-Configuration

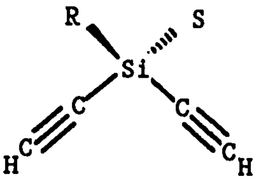
The molecule therefore may exist in one of the four stereoisomers noted as RR, RS, SR and SS which are found in identical abundance as determined by statistical law.



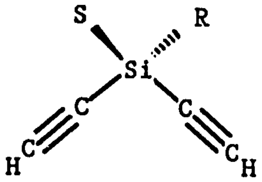
49 (RR)



50 (SS)



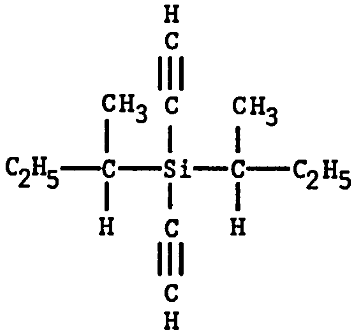
51 (RS)



52 (SR)

Of these four isomers (49-52), RR and SS is a pair of enantiomers while isomers RS and SR are the same molecule (mesomeric form). Although diastereomers are expected to have different physical properties, various efforts failed to separate them by high resolution GC and super critical fluid chromatography. In ^{29}Si NMR each pair of diastereomers (i.e., RR and SS, RS and SR) contribute one signal, so a doublet with 1:1 intensity ratio is expected in a nonchiral environment.

In the case of ^{13}C NMR spectrum, sec-butyl and ethynyl groups will be discussed separately. Sec-butyl groups in isomers RR and SS are chemical shift equivalent in a nonchiral solvent because of the existing 2-fold axis symmetry in each isomer and the mirror image relation between the two isomers. Similar reasoning stands for sec-butyl groups in isomers RS and SR. So a doublet resonance signal is expected for each carbon in sec-butyl group. Of the doublet, one signal is attributed to RR and SS pair while the other to RS and SR pair. The observed triplet resonance signal for each acetylenic carbon can be explained by recognizing that the two ethynyl groups in the isomer RS (or SR) are not equivalent. This is clearly shown in the following Fischer projection for the isomer RS.



The two ethynyl groups are diastereotopic, and two signals will occur corresponding to each ethynyl carbon in isomer RS and SR. However in isomer pair RR and SS, the two ethynyl groups are interchangeable due to an existing two fold axis symmetry. This will lead to one signal for each ethynyl carbon in isomers RR and SS. Overall a triplet (with 1:2:1 intensity ratio) for each ethynyl carbon in di(sec-butyl)diethynylsilane 47 is expected. The same reasoning also explains the triplet resonance signal observed for the acetylenic proton. The two dimension proton correlation spectrum (Figure 15) further confirms that the observed splitting on acetylenic proton is not due to a long range coupling but to the existence of stereoisomers.

Silyl-substituted acetylenic carbon atoms have chemical shifts in the normal region for carbon-carbon triple bonds. Based on the proton coupled ^{13}C NMR experiment, carbon at 95.66 ppm ($^1J_{CH}$=238 Hz) is protonated while signal at 83.97 ($^2J_{CH}$=41 Hz) is nonprotonated. Here C-1 carbon in $RC^{(1)}\equiv C^{(2)}H$ appeared upfield (i.e., with smaller chemical shift value in ppm) relative to C-2 carbon. This trend is opposite to what is observed in silyl-substituted vinyl systems[26] where C-1 carbon in $RC^{(1)}H=C^{(2)}H_2$ appears at downfield (larger chemical shift) relative to C-2 carbon. It has been reported that the deshielding[27] of the C-1 carbon in alkynes $RC^{(1)}\equiv C^{(2)}H$ depends on the nature of the substituted R groups and decreases in the order C>Si≥Ge. This is shown in Table 3.

Table 3. ^{13}C NMR chemical shifts of $RC^{(1)}\equiv C^{(2)}H$ (δ, ppm)[27]

Compounds	$C^{(1)}$	$C^{(2)}$
t-BuC≡CH	92.1	67.0
n-BuC≡CH	83.0	66.0
$Me_3SiC\equiv CH$	89.3	93.7
$Et_3SiC\equiv CH$	86.8	95.6
$Ph_3GeC\equiv CH$	84.6	96.6

Polymerization of $R_2Si(C\equiv CH)_2$ was carried out in the presence of $MoCl_5$ or WCl_6 catalyst in benzene or toluene solvent. The UV-visible absorptions and the molecular weights of the polymer products are summarized in Table 4. Polymers obtained by using WCl_6 catalyst have better

$$R_2Si(C{\equiv}CH)_2 \xrightarrow{MoCl_5 \text{ or } WCl_6} \text{violet polymer}$$

R = sec-Bu 53, iso-Pr 54.

solubility in chloroform and other organic solvents. However, polymers obtained by using catalyst $MoCl_5$ have higher λ_{max} value in UV-visible absorptions and narrower polydispersity in molecular weights (Table 4). When lower monomer concentration (experiment 3 in Table 4) was used, both λ_{max} in UV and the molecular weight was decreased significantly.

Table 4. Polymerization of $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$ 47 and $(iso\text{-}Pr)_2Si(C{\equiv}CH)_2$ 48

No.	Monomer	Cat.	Solvent	UV-visible[a] λ_{max}	Mw	PDI (Mw/Mn)
1	47	$MoCl_5$	benzene	565, 600	63,656	1.81
2	47	WCl_6	toluene	550, 600	66,335	2.45
3[b]	47	WCl_6	toluene	470, 500	16,514	1.95
4	48	$MoCl_5$	benzene	550, 600	32,255	4.09
5	48	WCl_6	toluene	546, 590	10,231	5.51

[a] UV spectra were taken in THF solvent.

[b] 50% lower monomer concentration was used.

In order to determine whether the polymerization proceeded through a chain mechanism or a stepwise mechanism, the polymerization of $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$ was followed by a GPC. The polymerization was carried out in toluene solvent. The result is shown in Figure 18. The sharp negative peak in the GPC chromatogram is originating from monomer since it has a smaller refractive index than the eluent toluene.

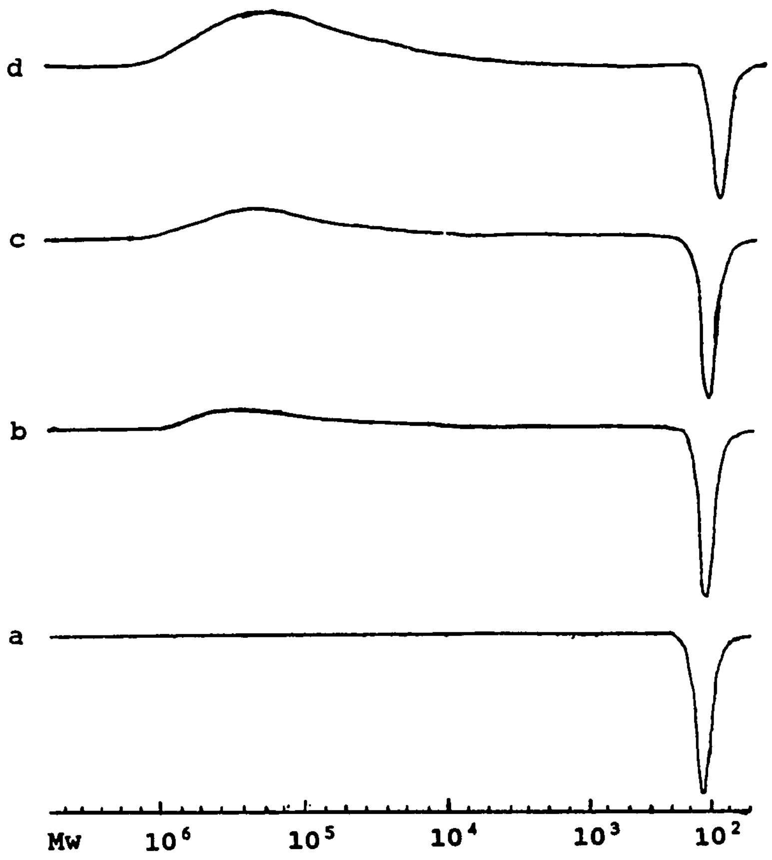


Figure 18. GPC chromatograms of polymerization products of di(sec-Bu)$_2$Si(C≡CH)$_2$ in presence of $MoCl_5$ at 50°C with different length of reaction time: (a) 40 minutes, (b) 2 hours, (c) 5.5 hours, (d) 10 hours

From a quantitative view of point, the negative monomer peak in Figure 18 can serve as a internal standard since the peak area still reflects the relative amount of the monomer left in the system. It is clearly seen that a significant amount of polymer was formed after two hours, and the amount of the polymer was increased as the reaction proceeded further. The feature that the molecular weight does not change with reaction time strongly suggests that the polymerization proceed by a chain mechanism.

More structural information was obtained by spectroscopic analysis. Solid state ^{29}Si NMR of both violet polymers <u>53</u> and <u>54</u> (prepared by using $MoCl_5$ catalyst) revealed sharp resonance signals which are shown in Figure 19. The top spectrum in Figure 19 is corresponding to violet polymer <u>54</u> while the bottom one to violet polymer <u>53</u>. Except slight difference in chemical shifts (ca. 2 ppm due to different substitutes on silicon atom), an essentially same pattern was developed in the ^{29}Si NMR for both polymers. This suggests that same structures exist in both polymers <u>53</u> and <u>54</u>.

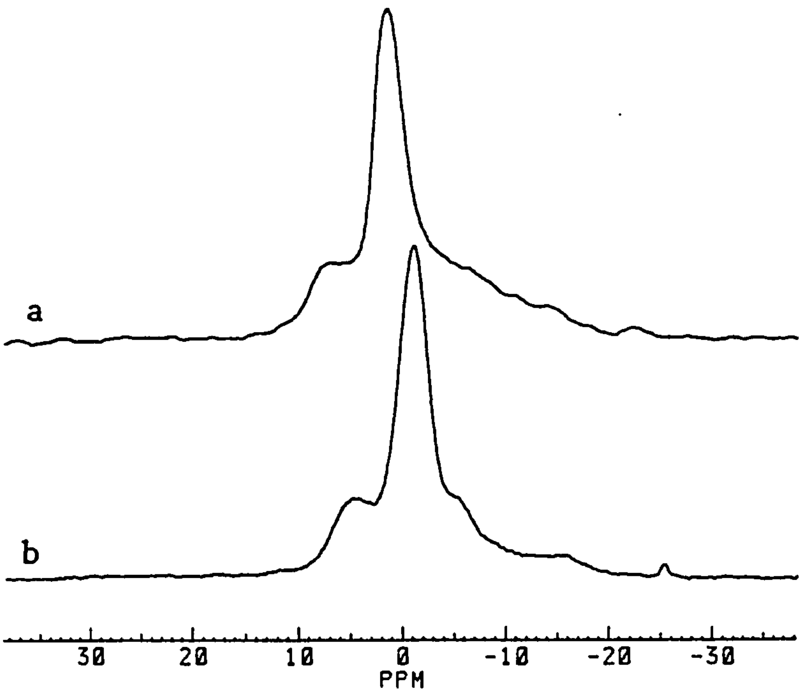


Figure 19. CPMAS ^{29}Si NMR spectra of violet polymer from $R_2Si(C{\equiv}CH)_2$ and $MoCl_5$ cat.: (a) R = iso-Pr 54, (b) R = sec-Bu 53

The broad peaks in Figure 19 are further resolved in the high resolution liquid state ^{29}Si NMR which is shown in Figure 20. The similarity between the solid and liquid state spectra (Figures 19(b) and 20(a)) of violet polymer 53 from $MoCl_5$ catalyst further confirms the good solubility of the polymer and implies that the signals observed in the liquid state NMR are complete (not partial signals due to solubilities).

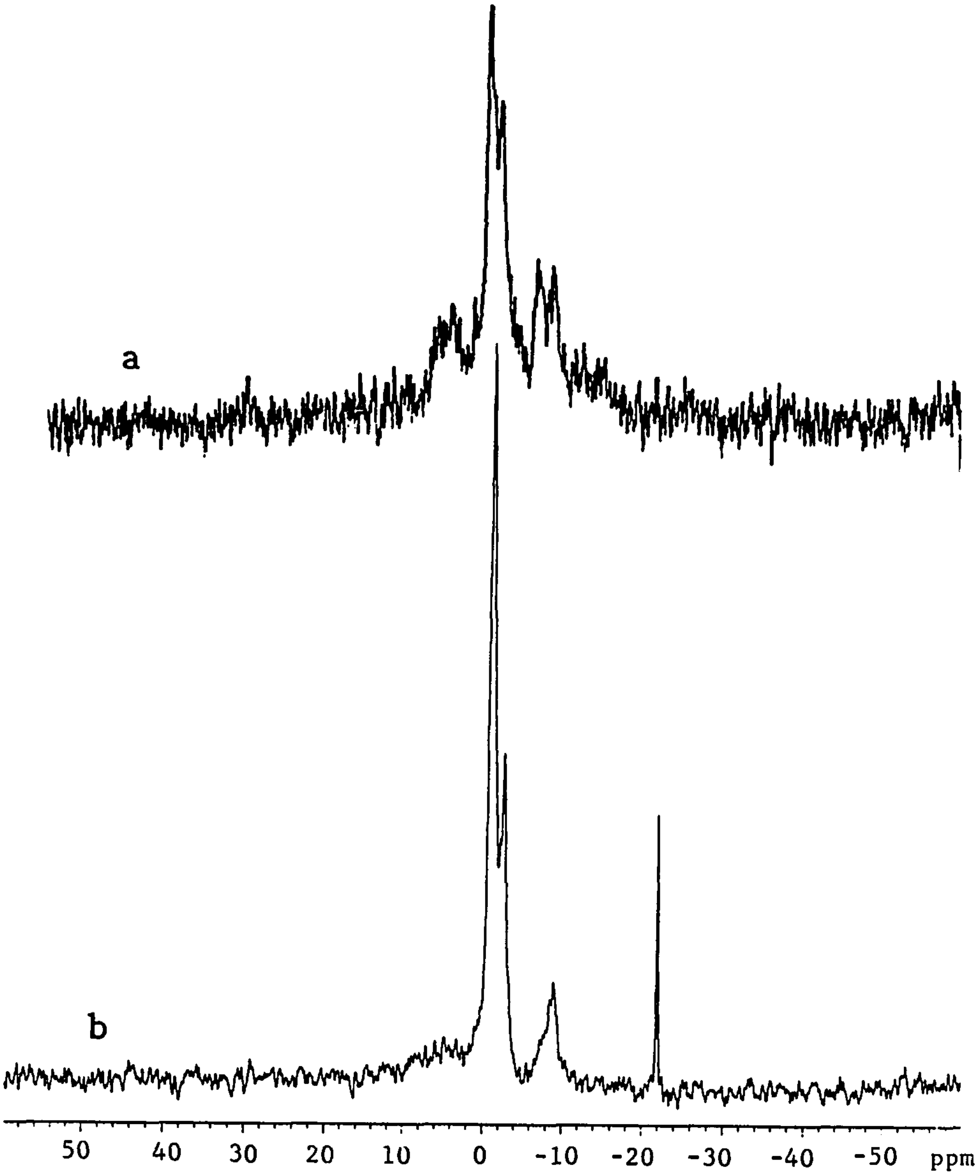


Figure 20. Liquid state quantitative ^{29}Si NMR spectrum of polymers 53 from $(sec\text{-}Bu)_2Si(C\equiv CH)_2$ by using catalyst $MoCl_5$ (a) or WCl_6(b)

By using different catalysts in the polymerization of $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$, polymers with a striking difference in the structural regularity was observed. Comparison of the polymer products from the catalysts $MoCl_5$ and WCl_6 are shown in the ^{29}Si NMR spectra in Figure 20. In Figure 20(b), the sharp peak at ca. -22 ppm is coming from silicon grease impurity introduced during the reaction. Since the sharp resonance signal occurring at ca. -1 ppm corresponds to a regular structure unit in the polymer, the content of the regular structure has been greatly increased by using WCl_6 catalyst.

The ^{13}C NMR spectrum of the violet polymer 53 (shown in Figure 21) allows us to examine the structure of polyacetylene backbone. Broad resonance signals between

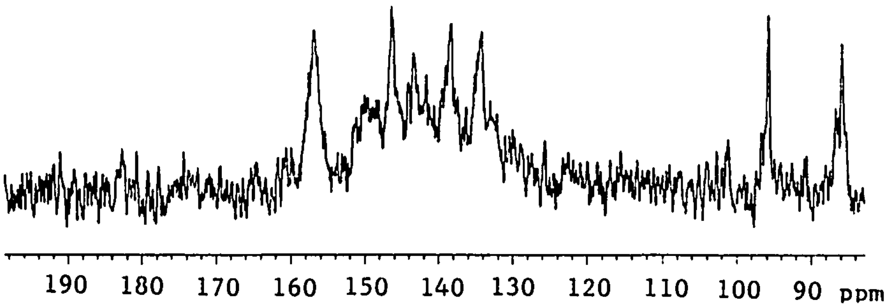
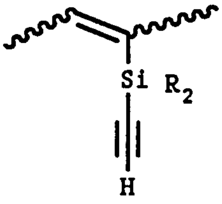


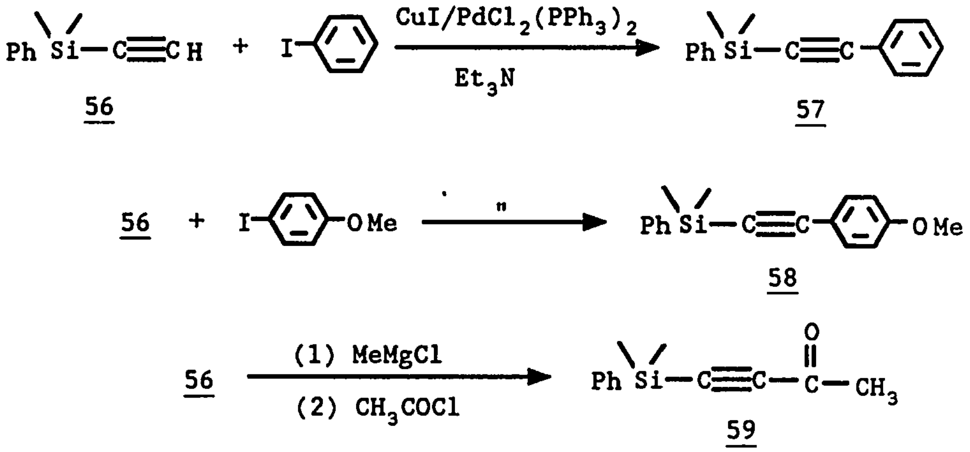
Figure 21. Quantitative ^{13}C NMR spectrum ($CDCl_3$ solvent) of violet polymer 53 from $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$ and WCl_6 catalyst. Alkyl region is not shown

130-160 ppm and many overlapping peaks imply a complicated structure existing in the violet polymers. Resonance signals at ca. 86 ppm and 96 ppm are coming from the dangling acetylene in the polymer structure. Clearly the following structural unit 55 is one of the components in the polymer structure.



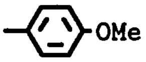
55

One of the key steps in characterizing the polymer structure is to identify the silicon atoms which are connected to the dangling acetylene, i.e., to assign the peak corresponding to the structural unit 55 in the ^{29}Si NMR spectrum in Figure 20. A perturbation is expected on silicon atom when the acetylenic hydrogen is replaced by another functional group. Compound phenyldimethylethynysilane, $PhMe_2SiC{\equiv}CH$ 56, has been chosen as a model compound in this study on purpose to find a suitable group R which will cause a significant upfield shift effect. Several derivatives of $PhMe_2SiC{\equiv}CH$ were synthesized as shown below:

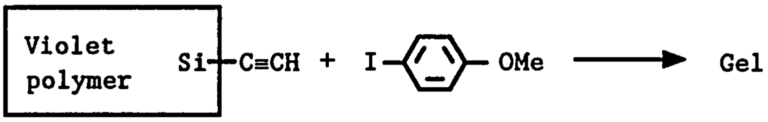


The ^{29}Si NMR chemical shift values of these compounds are listed in Table 5. An electron-withdrawing group like acetyl will cause a deshielding effect (downfield shift), while electron-donating groups will increase the shielding on silicon nuclei (upfield shift). In the case of the anisole group (compound 58), an upfield shift as large as 1.65 ppm has been observed. However, an attempt to use this result under the same conditions as for the violet polymer 53 was not successful due to the

Table 5. ^{29}Si and ^{13}C NMR of $PhMe_2SiC{\equiv}C\text{-}R$ (δ, ppm)

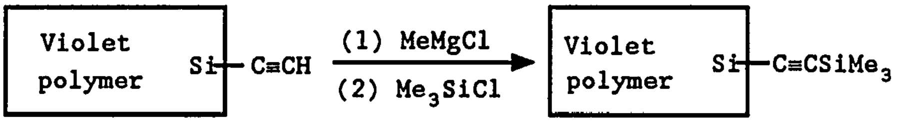
R	^{29}Si NMR	^{13}C NMR (acetylenic)
-H	-21.07	88.14, 94.82
$\text{-}COCH_3$	-20.65	87.28, 103.93
	-21.537	91.09, 105.89
	-22.72	

insolubility of the product.



53

Structural unit 55 was finally characterized by introducing a trimethylsilyl moiety on the dangling acetylene. Thus violet polymer 53 was reacted with excess methylmagnesium chloride in a THF solvent, then quenched with excess chlorotrimethylsilane. The obtained polymer 60 had similar solubility as 53. The ^{29}Si NMR spectrum of polymer 60 is shown in figure 22. As with most of reactions on polymer substrates, the above reaction was not complete as shown in the ^{13}C NMR spectrum. The incomplete reaction might originate from the first step, i.e., incomplete anion formation, where a strong electrostatic repulsion of the anion on polymer toward MeMgCl reagent will retard or even stop the further reaction (normally stop at about 70% conversion[28]).



53 60

In Figure 22, the sharp signal at ca. -19 ppm is the trimethylsilyl group. Comparing with Figure 20(b), ^{29}Si resonance signal at ca. -9 ppm was broadened after the dangling acetylene was blocked by trimethylsilyl group.

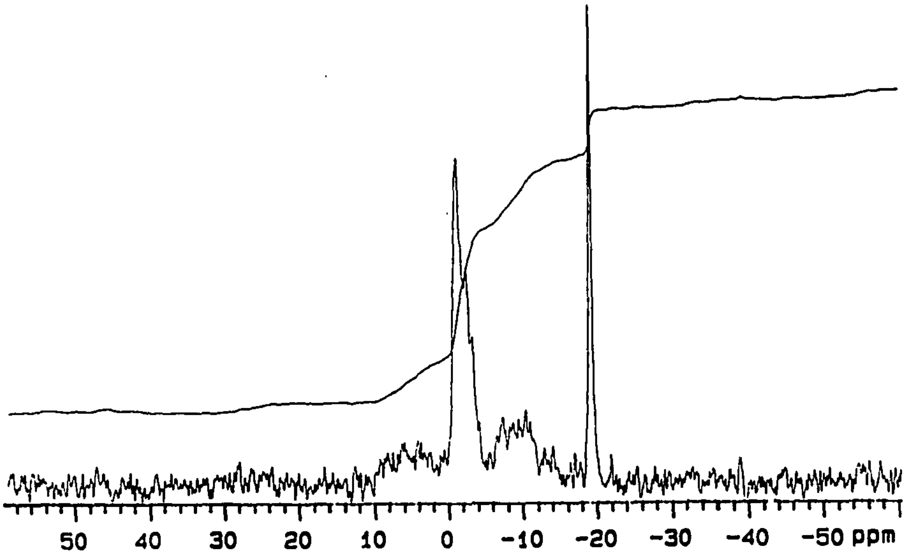


Figure 22. Quantitative ^{29}Si NMR spectrum of polymer <u>60</u>

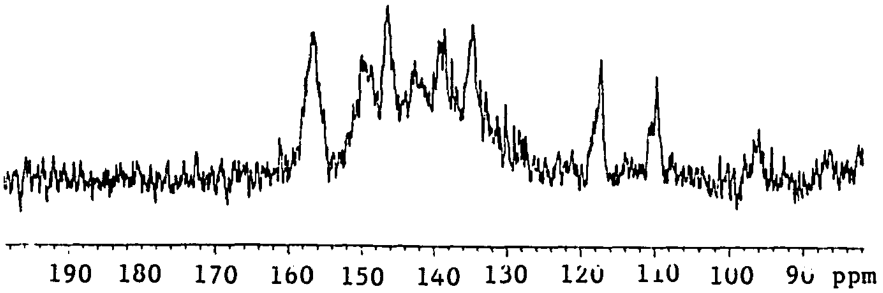


Figure 23. Quantitative ^{13}C NMR spectrum of polymer <u>60</u>

(the alkyl region is not shown)

This observation suggests that the broad signal at ca. -9 ppm corresponds to the structural unit 55. This is further confirmed by quantitative correlations between ^{29}Si and ^{13}C NMR spectra. Integral intensities of ^{29}Si NMR in Figure 22 are listed in Table 6. If the broad signal from 10 to 0 ppm, i.e., peak 1 in Table 6, is responsible for structural unit 55, all of the ethynyl groups should be functionalized to trimethylsilylethynyl groups in 100% conversion. This is not consistent with the ^{13}C NMR results where signals at ca. 86 and 96 ppm indicate an incomplete reaction. Based on the assumption that the broad resonance signal from -5 to -15 ppm comes from structural unit 55, the conversion of the reaction can be easily calculated from the integral intensity as shown below.

Table 6. Integration of ^{29}Si NMR in figure 22.

	Peak 1	Peak 2	Structural unit 55	Me_3Si group
Chemical shift range (ppm)	10 ~ 0	0 ~ -5	-5 ~ -15	-18 ~ -21
Integration[a]	13	35	18.7	13

[a] Integration is expressed in relative area.

In Figure 23, signals at ca. 110 and 117.5 ppm are from the functionalized disubstituted acetylene. The

$$R\text{-}C{\equiv}CH \longrightarrow R\text{-}C{\equiv}C\text{-}SiMe_3$$

$$\begin{array}{l}\text{The conversion} \\ \text{(from } ^{29}\text{Si NMR)}\end{array} = \frac{13}{18.7} = 69.5\%$$

relatively weak signals at ca. 86 and 96 ppm correspond to the unreacted monosubstituted acetylene. Integral intensities of ^{13}C NMR in figure 23 are summarized in Table 7. The conversion can be calculated by two methods: (1) integration ratio between monosubstituted acetylene and disubstituted acetylene, and (2) integration ratio between acetylenic carbons and Si-Me carbons. The calculations are shown as follows. Conversion from both calculations are consistent with the result obtained from ^{29}Si NMR within experimental error. This consistence between ^{13}C and ^{29}Si NMR results finally confirms the assignment that the resonance signal at -9 ppm in Figure 22 is from the structure unit <u>55</u>.

Table 7. Integration of ^{13}C NMR in figure 23.

	acetylenic carbons		$Si\text{-}Me_3$
	$R\text{-}C{\equiv}C\text{-}SiMe_3$	$R\text{-}C{\equiv}CH$	
Chemical shift range (ppm)	107~120	84~100	-2~2
Integration[a]	67.12	31.55	106.12

[a] Integration is expressed in relative area.

Since all of the silicon nuclei containing dangling acetylene group can be explained by the broad peak

$$\text{R-C}\equiv\text{CH} \longrightarrow \text{R-C}\equiv\text{C-SiMe}_3$$

The conversion from ^{13}C NMR:

Method (1):

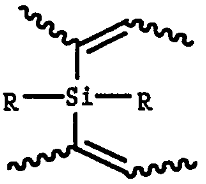
$$\frac{\text{C's from R-C}\equiv\text{C-SiMe}_3}{\text{all acetylenic C's}} = \frac{67.12}{67.12 + 31.55} = 68\%$$

Method (2):

$$\frac{\text{C's from SiMe}_3}{\text{C's from all C}\equiv\text{C}} \times \frac{2}{3} = \frac{106.12}{67.12 + 31.55} \times \frac{2}{3}$$

$$= 71.7\%$$

centered at ca. -9 ppm, all the resonance signals from 10 to -5 ppm in Figure 20 must come from silicon nuclei which are connected to two vinyl carbons. This statement contains a reasonable assumption that except for the transformation of triple bonds into double bonds, no Si-C bond will be cleaved during the polymerization in the presence of a metathesis catalyst. The sharp resonance at ca. -1 ppm belongs to the regular structure, i.e., 3-, 4-, or 5-membered ring structure. The broad resonance signal between 10-0 ppm in Figure 20 is assigned to a branch unit 61. The extreme broadening resonance here



61

can be explained by the restricted motion in this polymer which will cause a significant line broading[29].

In the ^{13}C NMR spectrum of violet polymer 53 (Figure 21), it is interesting to note that a signal at 157 ppm is well separated from the rest of the vinyl carbons. This carbon is shown to be nonprotonated by the comparison of a proton-coupled ^{13}C spectrum with a ^1H gated decoupled ^{13}C spectrum which is shown in Figure 24. Lack of broadening in the proton-coupled ^{13}C NMR spectrum suggests the carbon at ca. 157 ppm solely consists of nonprotonated carbons.

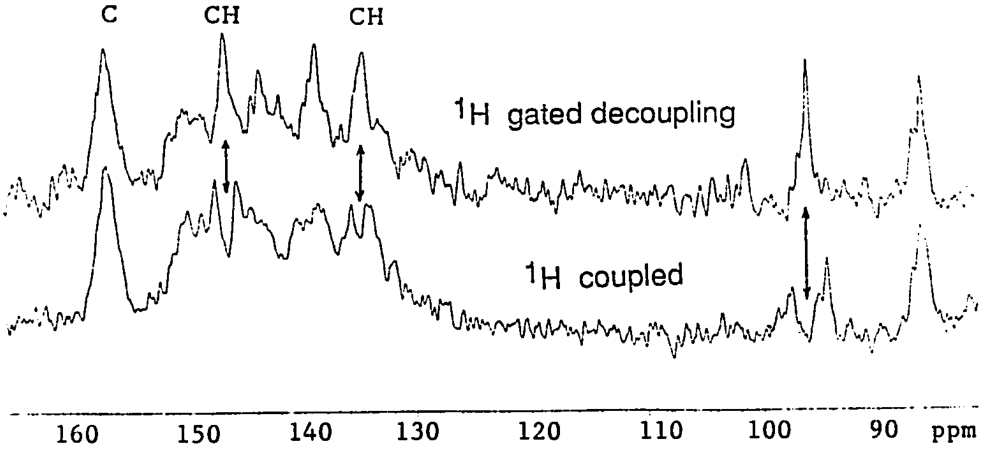
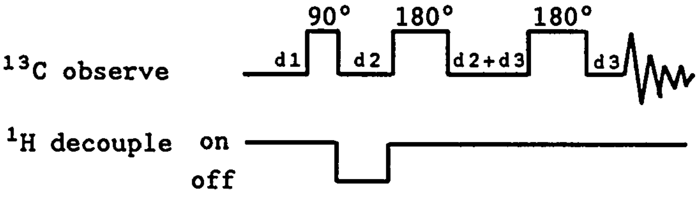


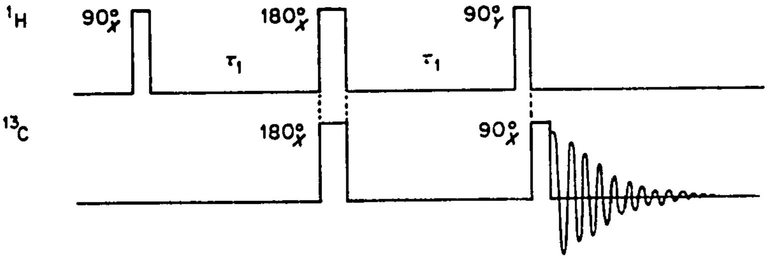
Figure 24. Comparison between ^1H coupled ^{13}C NMR (bottom) and gate-decoupled ^{13}C NMR spectrum (top) of the polymer 53 from WCl_6 catalyst

Substituted silicon-containing polyacetylene[18,30] normally have two peaks in ^{13}C NMR in vinyl carbon region (chemical shift value less than 150) with a peak width at half height ($W_{1/2}$) of ca. 4 ppm. In Figure 24, $W_{1/2}$ for peak at 157 ppm is only ca. 2 ppm. The narrower peak width in violet polymer further indicates a defined structure in the polymer.

In order to further distinguish the nonprotonated carbon in the vinyl carbon region, APT (Attached Proton Test) pulse sequence was used to selectively observe the non-protonated vinyl carbons. The principle of the APT experiment[31] is shown in the following pulse sequence schematically. Following a 90° observation pulse on ^{13}C channel, ^{13}C nuclei are allowed to couple with ^{1}H by turning off the decoupler for a short period of time d2 (= 1/(2J)). During this period, protonated carbons (CH) will be fanned out while quaternary carbons are not affected. The spectrum is acquired after two 180° pulses which are used to refocus the signal. In our experiment, d1=10 seconds, d2=0.003 second (J_{CH}=150 Hz) and d3=0.001 second were used to acquire the spectrum.



INEPT (Insensitive Nucleus Enhancement by Polarization Transfer) sequence was also used in our study. In its simplest version the INEPT experiment[31] can be summarized by the following pulse sequences.



The delay τ_1 is determined by the magnitude of $^1J_{CH}$ according to equation $\tau_1=1/(4J)$. Since in this experiment the relaxation process is governed by the proton polarization transfer, a much shorter repetition time can be used. In our experiment a repetition time of 3 seconds and J constant of 150 Hz were used. The resulted enhancement in protonated carbons due to the proton polarization transfer and suppression for quaternary carbons together allow us to selectively observe the protonated vinyl carbons.

To our surprise, in the presence of the relaxation reagent Cr(acac)$_3$ no signals in the vinyl region were observed in both APT and INEPT experiments. The failure to obtain signals can be explained when nuclear relaxation process is considered. In the presence of a relaxation reagent, the relaxation process is greatly accelerated. The nuclei may relax back to ground state during the signal refocusing period in both APT and INEPT sequences. So using the same parameter, spectra with good signal-to-noise ratio were obtained as shown in Figure 25.

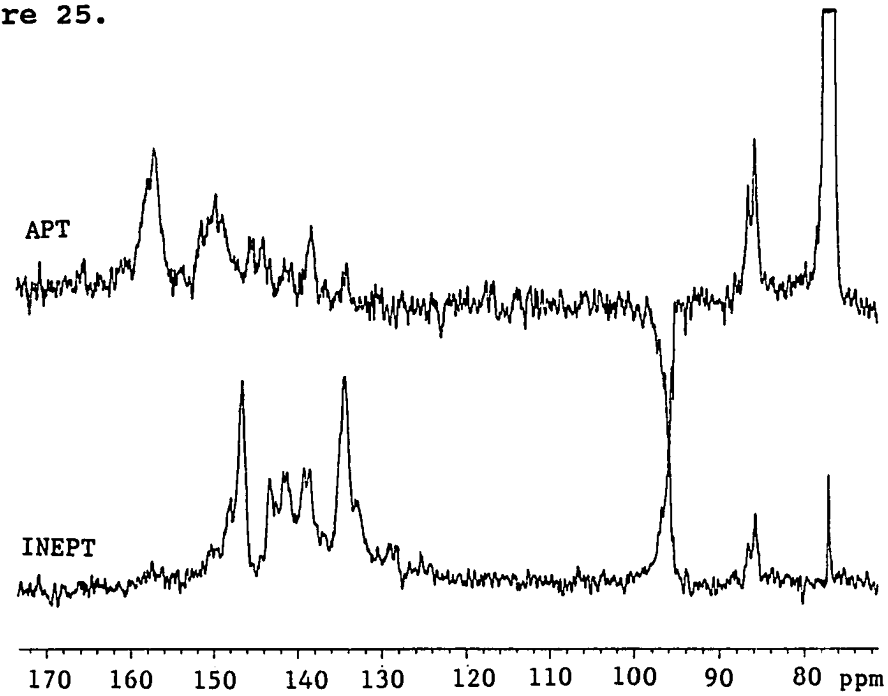
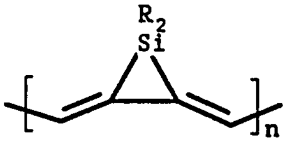


Figure 25. The refocused APT (top) and the INEPT (bottom) ^{13}C NMR spectra of the polymer 53 ($CDCl_3$) from $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$ and WCl_6 catalyst

In the APT spectrum two quaternary vinyl carbons were detected at ca. 157 and 149 ppm with a intensity ratio of about 1:1. The INEPT spectrum revealed two major protonated vinyl carbons at ca. 146 and 134 ppm which overlapped several minor peaks in between. The completely collapsed $CDCl_3$ solvent signal (the weak singlet peak at 77 ppm is due to the $CHCl_3$ residue), together with the complete disappearance of the signal at 157 ppm in the INEPT spectrum again confirm that the signal at 157 ppm solely consists of a quaternary carbon.

Based on the relatively narrow peak width ($W_{1/2}$ ca. 2 ppm) and the symmetric peak shape, ^{13}C resonance signal at ca. 157 ppm in Figure 21 represents one type of non-protonated carbon in the repeating unit of the polymer. The percentage of this carbon among all vinyl and acetylenic carbons allows us to extrapolate the mole percentage of the repeating unit. Previous discussion has concluded that only three-, four- and five-membered ring structures are possible for the cyclopolymerization. These ring structures are listed as follow.



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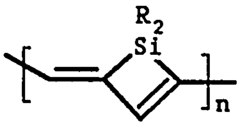

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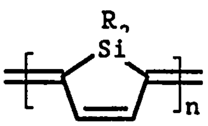


24

If we define "A" as the percentage of the area of the 157 peak among all of the vinyl and acetylenic carbons, i.e.,

$$A = \frac{\text{Carbon at 157 ppm in } ^{13}\text{C NMR}}{\text{All carbons for C}{=}\text{C and C}{\equiv}\text{C}} \qquad (2)$$

The mole percentage of the repeating unit can be calculated from the following equation:

$$\text{Mole percentage of repeating unit} = A \times M \qquad (3)$$

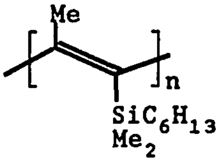
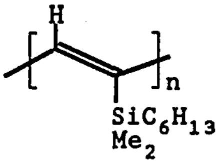
Here "M" is the number of different vinyl carbons in the repeating unit. For the four-membered ring 23, M equals four. While in the three- and five-membered rings, i.e., 22 and 24, M equals two. The mole percentages of the repeating unit from the equation (3) are listed in Table 8. Comparison of these calculated results (from ^{13}C NMR) with the one from ^{29}Si NMR clearly shows that only the four-membered ring structure 23 is consistent with what is observed in ^{29}Si NMR within experimental error.

Table 8. Correlation between quantative ^{13}C and ^{29}Si NMR data

A(%)	mole % of repeating unit from ^{13}C NMR		mole % of repeating unit from ^{29}Si NMR	polymer
	M=2	M=4		
15.5	31	62	65	R=sec-Bu WCl_6
11.3	22.6	45.2	44.2	R=iso-Pr WCl_6

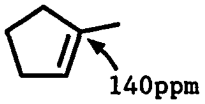
A chemical shift value of 157 ppm is far more downfield than any of the vinyl carbons observed so far in conjugated polyacetylene-type polymers which are summarized in Table 9. Although ^{13}C nuclei signals in

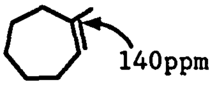
Table 9. ^{13}C chemical shift values for polyacetylenes

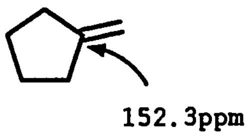
Polymer name	Vinyl carbon (ppm)	Reference
cis-polyacetylene	126-129	32
trans-polyacetylene	136-139	32
polythienylene (polythiophene)	110,120	33
polypyrole	105,123	34
	131.3, 140	30
	137,147	18

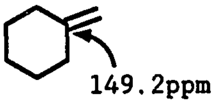
silyl-substituted polyacetylenes will occur slightly downfield, the chemical shift values are still below 147 ppm. The unusual downfield shift of the ^{13}C nucleus to 157 ppm in the violet polymer implies a new structural unit.

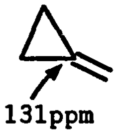
It is known[35,36] that vinyl ^{13}C nuclei in exo-methylenecycloalkanes will occur at ca. 10 ppm down field relative to their cyclic olefin analogues. Some examples are listed below.

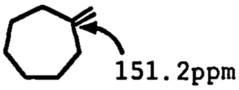






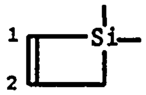
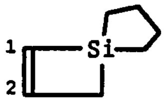
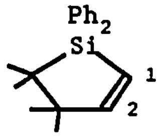
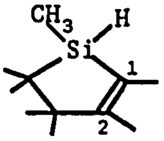






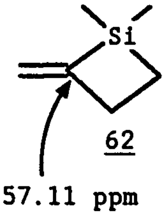
Some vinyl ^{13}C chemical shift values in silacyclic alkenes are shown in Table 10. Substitutes on the silicon atom have a negligible effect on the vinyl carbon at β position, i.e. C-2 carbon in Table 10 (entry 2,3). In contrast to the vinyl carbons in cycloalkenes where cyclopropene has a much smaller shift value (108.7 ppm) than cyclobutene (137.2 ppm) and cyclopentene (130.8 ppm), the chemical shift values of vinyl carbons in silacycloalkenes are less affected by the ring size.

Table 10. Vinyl ^{13}C chemical shift values of silacyclic alkenes

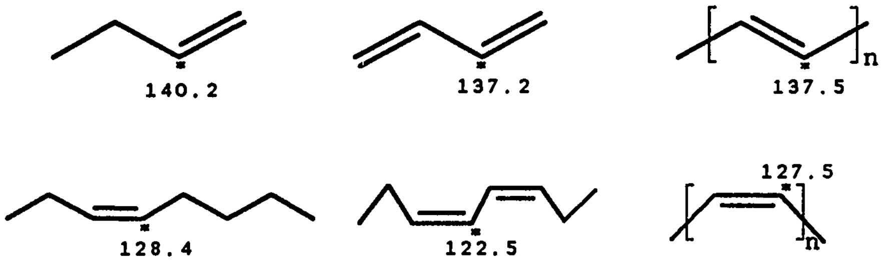
Entry	Compounds	δc		References
		C-1	C-2	
1		152		37
2		142	152	38
3		139.3	152.9	38
4		133.4	155.1	39
5		131.3	153.9	39

From entries 2 and 3 in Table 10, it is seen that the ^{13}C chemical shift for carbon α to Si (C-1) is only slightly affected by different alkyl substituents on silicon atom.

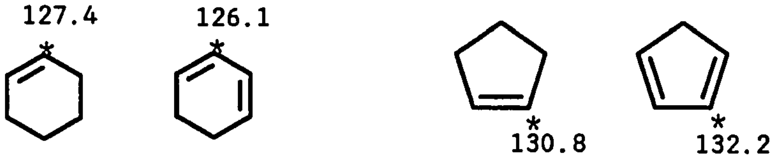
Conlin et al.[40] recently reported the ^{13}C chemical shift values for 2-methylene-1,1-dimethylsilacyclobutane 62. Since the influence of the substitutes on Si atom toward the chemical shift of the carbon α to silicon is negligible (previous discussion), the compound 62 can serve as an approximate model for the four-membered ring structure 23. This assumption is further supported by the negligible conjugation influence[41] on the ^{13}C NMR chemical shift value. Although the decrease in bonding order arising from multiple bonds in conjugated π-systems results in a shielding of the central carbon atoms, this effect is not significant when a monoene is extended to a polyene system. This is clearly seen by the following comparison. In the first row are listed 1-butene, 1,3-butadiene and trans-polyacetylene. Only ca. 3 ppm shift is observed in the case of trans double bond from



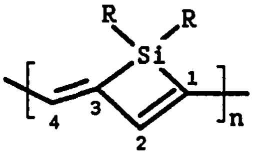
62



monoene to polyene. In the case of a cis-double bond, even less shift (ca. 1 ppm) is observed (second row). Extending conjugation in cycloalkenes[35] normally will cause a similar shielding effect as in the linear case, however, a deshielding effect is observed in some cases (as in cyclopentadiene).



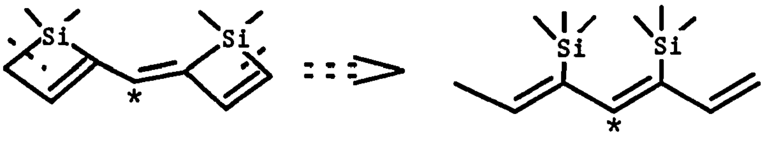
In the previous study, two nonprotonated carbons (at ca. 157 and 149 ppm) and two protonated vinyl carbons (at ca. 146 and 134 ppm) are found in the violet polymer. If the model compound <u>62</u> is proper for the ring structure <u>23</u>, the C-3 should occur at ca. 157 ppm. Another nonprotonated carbon is C-1 which is at ca. 149 ppm. The chemical shift difference between C-1 and C-3 is 8 ppm which is consistent with what is observed between exo-cyclic double bonds and corresponding cycloalkenes[35,36]. Carbon C-4 is assigned to 134 ppm



23

C-1: 149ppm
C-3: 157ppm
C-2: 146ppm
C-4: 134ppm

based on the following consideration. By opening the Si-C bonds in the four-membered ring of the model compound 63, a simplified model compound 64 is obtained. The chemical shift difference is negligible for C^* in model 63 and 64 since the C^* is not in the ring. From

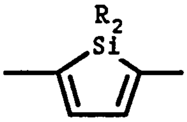


63

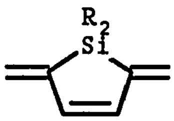
64

silyl substituted polyacetylene in Table 9, the chemical shift for C^* in the model compound 64 should occur at ca. 137 ppm. So the assignment of 134 ppm to C-4 in 23 is reasonable. The chemical shift 146 ppm is assigned to C-2 according to the ^{13}C chemical shift values in silacyclobutene (Table 10, entry 2 and 3) and the conjugation influence[41] on chemical shift.

Although a mixture of the five-membered ring structures 65 and 66 could also account for the two non-protonated vinyl ^{13}C signals, they are discarded based on the following arguments:



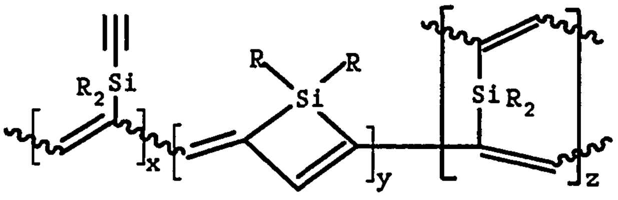
65



66

First, they can not explain the big chemical shift difference (12 ppm) between the two protonated vinyl carbons (CH). Secondly, a chemical shift of ^{13}C nucleus reflects the electron environment around the nucleus. If silole structures 65 and 66 were present, according to the big chemical shift difference (ca. 8 ppm) between the two nonprotonated carbons, one would expect at least a similar difference in the ^{29}Si chemical shift. However the observed sharp peak with $W_{1/2}$ ca. 2 ppm is inconsistent with what is predicted from a mixture of 65 and 66.

In summary for the chemical structure of the violet polymer, three structural units 23, 55 and 61 have been identified. The structure for violet polymer is proposed as follows. The contents of each unit in the violet polymers are summarized in Table 11.



55 23 61

Table 11. Contents of structural units in the violet polymer

$$R_2Si(C{\equiv}CH)_2 \xrightarrow{\text{catalyst}} \text{violet polymer}$$

R	Catalyst	Mole % of structural units^a(%)		
		55	23	61
Sec-Bu	$MoCl_5$	32	42	26
Sec-Bu	WCl_6	15	65	20
iso-Pr	WCl_6	39	44	17

^{a}Results are from quantitative ^{29}Si NMR data.

Catalytic Polymerization of (n-alkyl)$_2$Si(C≡CH)$_2$

In order to study the steric effect of less bulky substitutes on silicon atom on the polymerization of diethynylsilanes, several n-alkyl-substituted diethynylsilanes were synthesized as follows:

$$\mathrm{RMgBr} + \mathrm{SiCl_4} \xrightarrow{\text{Hexane}} \mathrm{R_2SiCl_2} + \mathrm{MgX_2}\downarrow$$

$$2\ \mathrm{HC{\equiv}CMgCl} + \mathrm{R_2SiCl_2} \xrightarrow{\text{THF}} \mathrm{R_2Si(C{\equiv}CH)_2}$$

$R = CH_3$, 8
$n\text{-}C_3H_7$, 67
$n\text{-}C_4H_9$, 68
$n\text{-}C_6H_{13}$, 69

In contrast to the polymerization of the diphenyl-, di-sec-butyl and di-iso-propyldiethynylsilanes, the polymerization of dimethyldiethynylsilane always gave a violet-gel when Mo-based catalysts were used.

$$\mathrm{(CH_3)_2Si(C{\equiv}CH)_2} \xrightarrow{\text{cat.}} \text{violet gel}$$

Mo catalyst system: $Mo(CO)_6$-CCl_4-$h\nu$
or $MoCl_5$-THF
or $MoCl_5$-Benzene
W catalyst system: WCl_6-Toluene

Various efforts such as high dilution and lower reaction temperature failed to stop the gelation. Utilization of WCl_6 as catalyst afforded an insoluble polymer product at room temperature without the formation of gel.

Polymerization of $R_2Si(C{\equiv}CH)_2$ (67, 68, or 69) with $MoCl_5$ catalyst produced the polymer products which were blue and revealed three sharp resonance signals in ^{29}Si NMR (Figure 26). The molecular weights and UV- visible absorptions of the polymer products are summarized in Table 12.

$$R_2Si(C\equiv CH)_2 \xrightarrow{MoCl_5} \text{blue polymer}$$

R = n-C_3H_7, 70
n-C_4H_9, 71
n-C_6H_{13}, 72

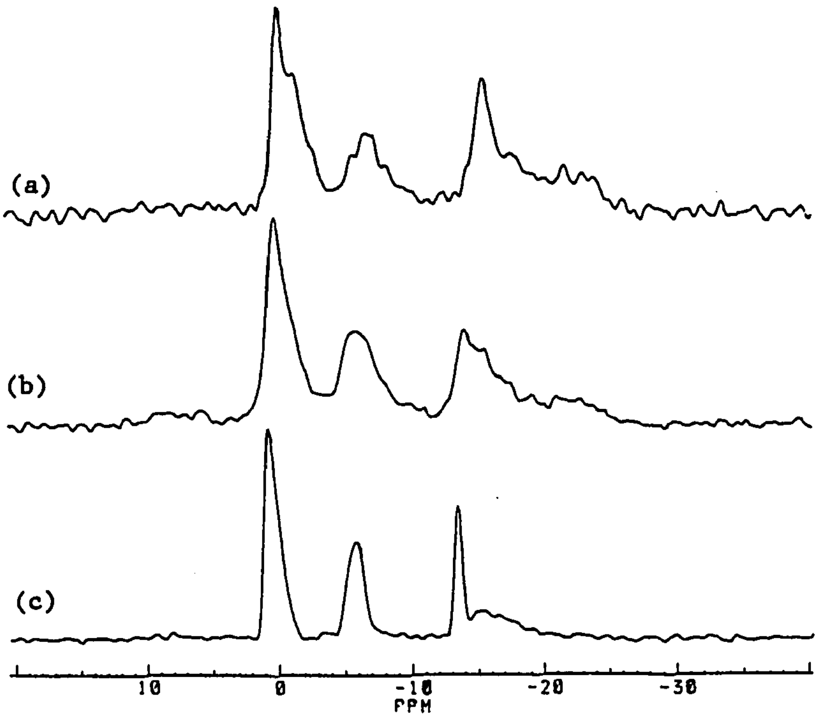


Figure 26. CP/MAS ^{29}Si NMR spectra of blue polymers with R equals n-propyl (a), n-butyl (b), and n-hexyl (c)

Table 12. Polymerization of di-n-alkyldiethynylsilane[a]

Monomer $R_2Si(C{\equiv}CH)_2$	Catalyst	Temp(°C)	UV-visible[b] λ_{max}	Mw	PDI
R= n-Pr	$MoCl_5$	25	570, 620	54,195	4.01
R= n-Bu	$MoCl_5$	50	570, 620	87,800	6.90
R= n-hexyl	$MoCl_5$	50	580, 620	123,440	5.81
"	$MoCl_5/Ph_4Sn$	25	584, 620	77,665	5.11
"[c]	$MoCl_5/Ph_4Sn$	25	580, 620	249,823	2.75

[a] Polymerization was performed in benzene solvent.
[b] UV spectra were taken in THF solvent.
[c] 50% higher monomer concentration was used in this case.

Polymerization of di-n-hexyldiethynylsilane 69 in the presence of WCl_6 catalyst, however, afforded a violet polymer product. The comparisons between the two polymers by using catalysts $MoCl_5$ or WCl_6 are shown in ^{29}Si NMR and UV-visible spectra (Figures 27 and 28). Clearly when WCl_6 catalyst was used, a more regular structure was developed during the polymerization. In the ^{13}C NMR spectrum of the di-n-hexyldiethynylsilane polymer from WCl_6 (Figure 29), the four distinct peaks at ca. 157, 150, 145 and 138 ppm are in a ratio of 1:1:1:1. These results suggest that the polymer from WCl_6 catalyst mainly consists of a four-membered ring. If the peak at ca. -6 ppm in ^{29}Si NMR (Figure 27) originates from the four-membered ring unit, the content of the four-membered ring in the polymer from $MoCl_5$ catalyst is quite low (only ca. 25%) based on the ^{29}Si NMR result.

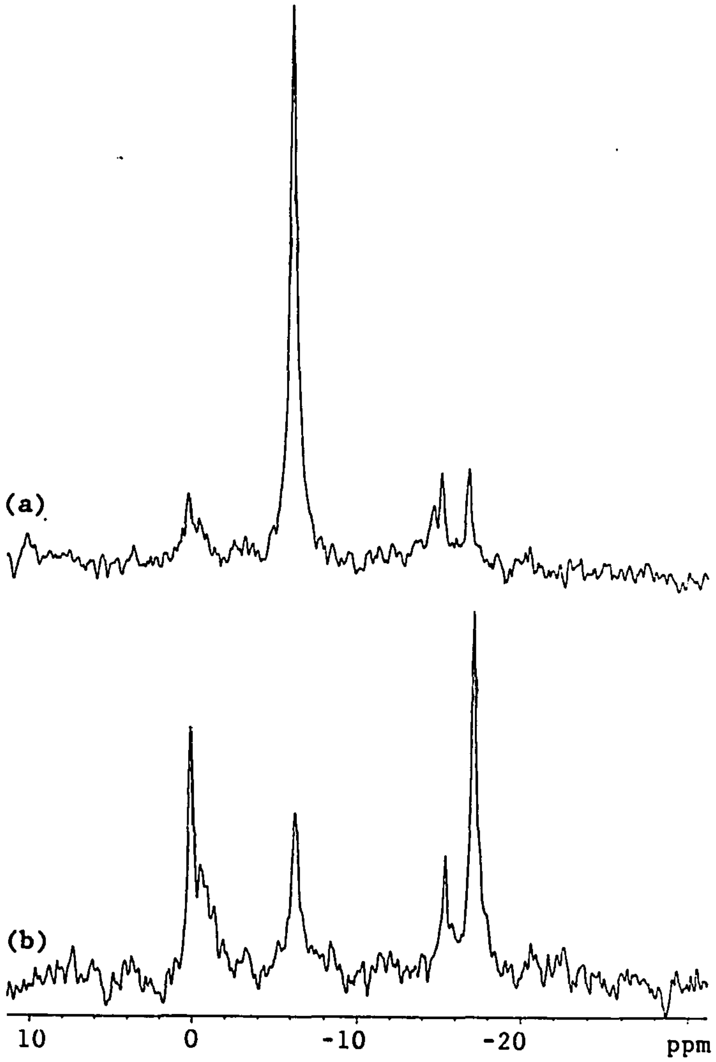


Figure 27. Quantitative ^{29}Si NMR spectra of di-n-hexyldiethynylsilane polymers by using (a) WCl_6 and (b) $MoCl_5$ catalyst

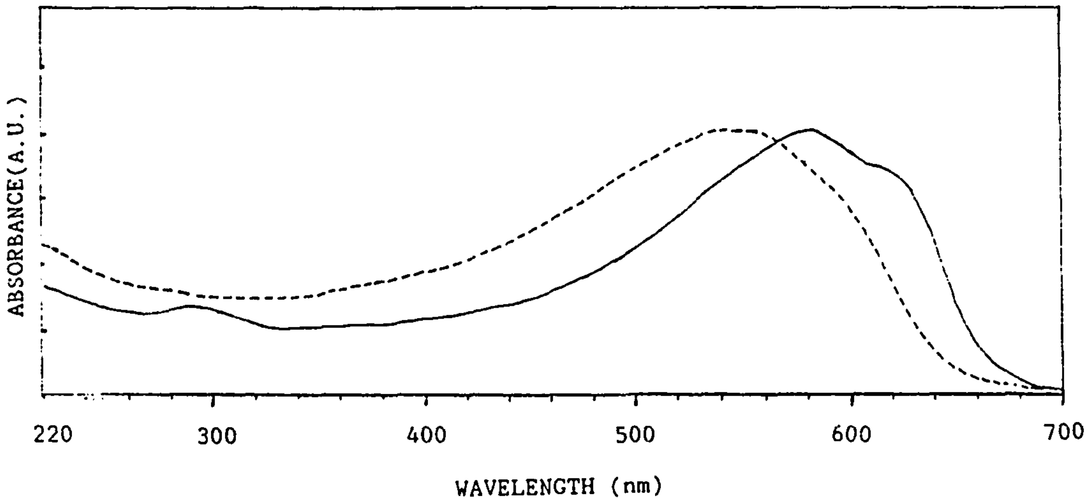


Figure 28. UV-visible spectra of di-n-hexyldiethynylsilane polymers from $MoCl_5$ catalyst (solid line) and WCl_6 catalyst (dotted line). Both spectra were measured in THF solvent

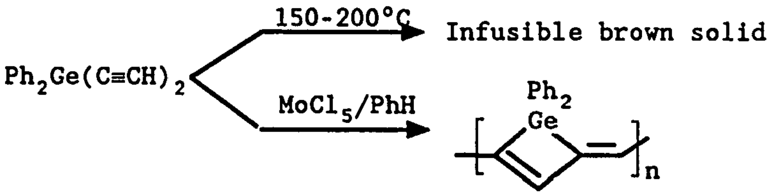
Figure 29. Quantitative ^{13}C NMR spectra of di-n-hexyldiethynylsilane polymers from WCl_6 catalyst (alkyl region not shown)

Miscellaneous

In order to extend the polymerization of diethynylsilane $R_2Si(C{\equiv}CH)_2$ to the germanium analogue, diphenyldiethynylgermane was synthesized as follows:

$$Ph_2GeCl_2 + 2\ HC{\equiv}CMgCl \xrightarrow{THF} \underset{\underline{73}}{Ph_2Ge(C{\equiv}CH)_2}$$

Thermal polymerization of diphenyldiethynylgermane 73 was first reported by Luneva et al.[3] where a clear, hard, brown solid was obtained with a softening point 120- 160°C. This polymer was soluble in benzene and hexane, and had a molecular weight of 4100. In our hands, however, heating diphenyldiethynylgermane 73 under the same condition resulted in an infusible brown solid. The difference might originate from the monomers possessing different purity. As expected, a violet polymer 74 was obtained by using $MoCl_5$ as catalyst. The UV-visible spectrum of the violet polymer 74 is shown in



Violet polymer 74
Mw-148,513; PDI-2.09

Figure 30. The structure of the polymer is assumed to be the four- membered ring in analogy to the corresponding silicon systems.

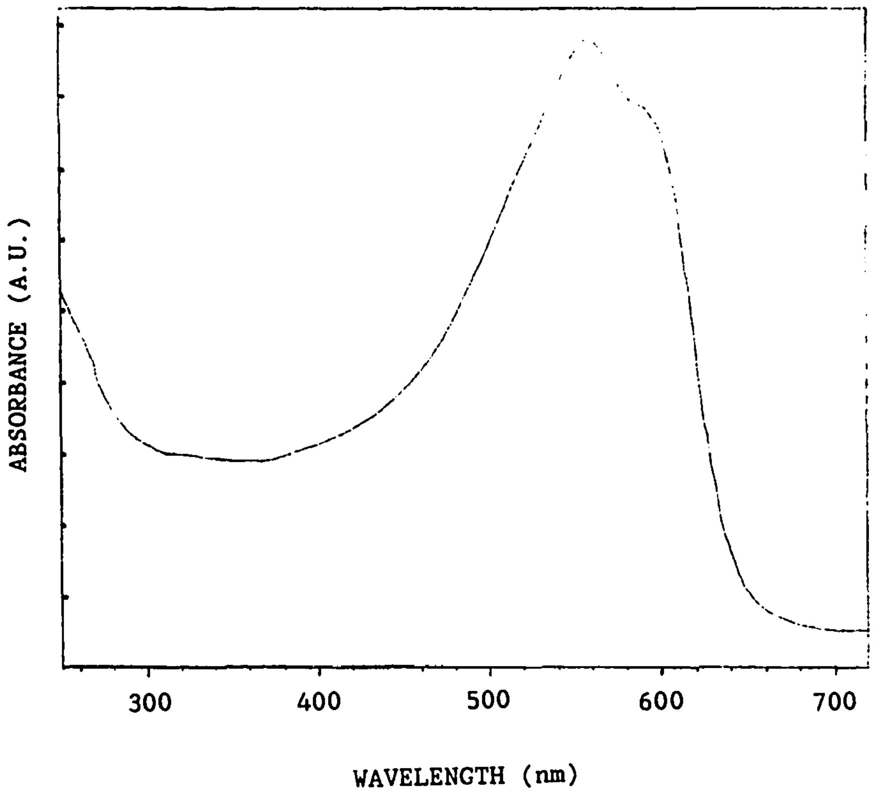
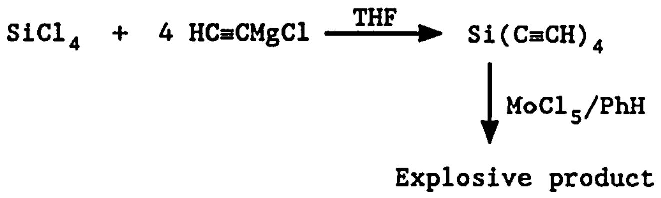


Figure 30. UV-visible spectrum of diphenyldiethynylgermane polymer 74 in THF solvent

Tetraethynylsilane was synthesized according to the literature[42] via the reaction of $SiCl_4$ with four equivalents of ethynylmagnesium chloride. Polymerization



$$\begin{tikzcd}[column sep=large] SiCl_4 + 4\,HC\equiv CMgCl \arrow[r, "THF"] & Si(C\equiv CH)_4 \arrow[d, "MoCl_5/PhH"] \\ & \text{Explosive product} \end{tikzcd}$$

of tetraethynylsilane at room temperature in the presence of $MoCl_5$ catalyst afforded a brown solid product. The solid product exploded either when grinding it in air or shaking it in a flask under an argon atmosphere. DSC (differential scanning calorimetry) of the solid product (Figure 31) indicated a highly exothermic reaction occurred after 50°C. The energy released during the explosion was as high as 16,970 J/g .

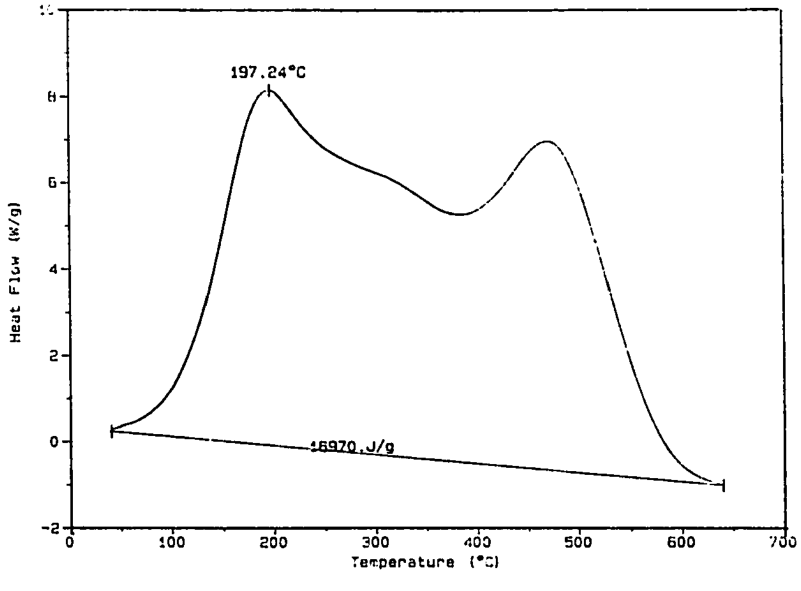
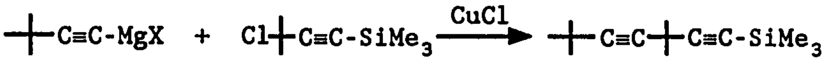


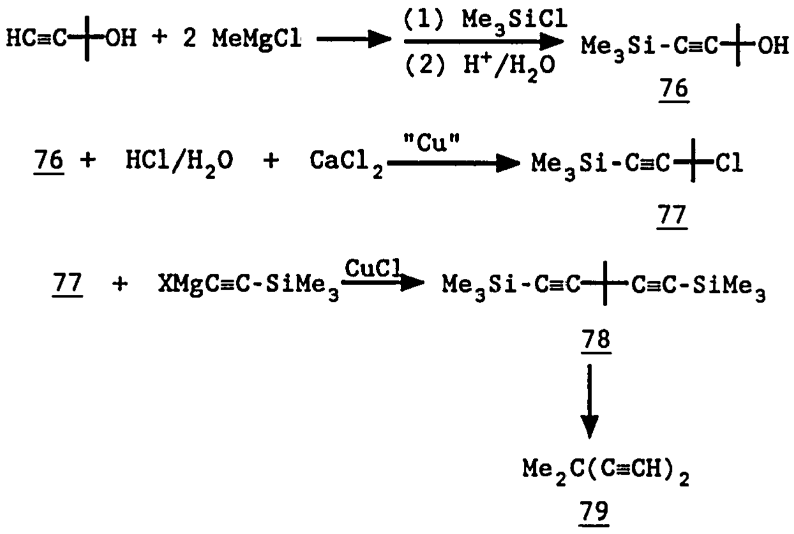
Figure 31. DSC of the tetraethynylsilane polymer (sample size: 2.1 mg; temperature program: 10°C/min.)

Scott et al.[43] reported a synthesis of "homoconjugated polyacetylenes" 75 via a CuCl-catalyzed coupling reaction between magnesium acetylide and tertiary propargylic chloride.

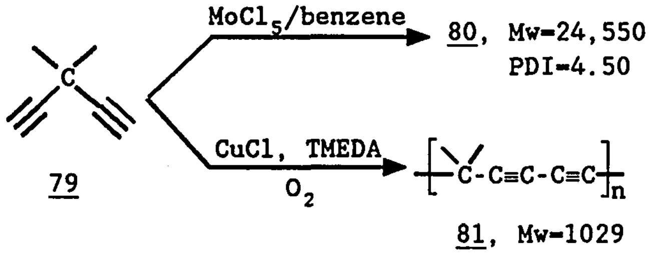


75

This coupling reaction was used to synthesize the 3,3-dimethylpenta-1,4-diyne 79. However this route did not work well for the synthesis of other 3,3-dialkylpenta-1,4-diyne due to the failure in the chlorination or coupling step.

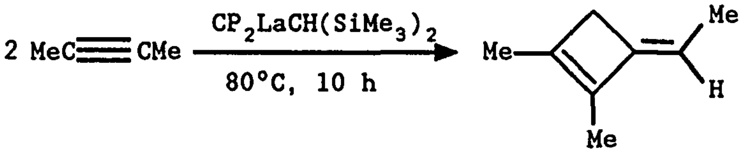


In contrast to the result obtained for silicon and germanium analogues, the polymerization of 3,3-dimethylpenta-1,4-diyne 79 in the presence of $MoCl_5$ catalyst did not produced a violet but rather a yellow-brown polymer 80. The UV-visible spectrum of the yellow-brown polymer exhibited a long tailing from 220 nm to 640 nm without showing any significant λ_{max} which implies a lack of a defined electronic structure in the polymer product.



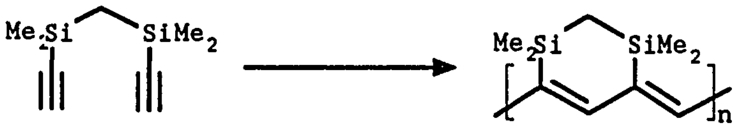
Oxidative coupling[44, 45] of terminal alkynes (Glaser Coupling) afforded a white polymer 81, poly(dimethylmethylenediacetylene), although molecular weight was not high.

The failure of the cyclopolymerization for the carbon analogue 79, 3,3-dimethylpenta-1,4-diyne, might be due to the instability of the cyclobutene repeating unit. Heeres et al.[46] recently reported the cyclodimerization of disubstituted alkynes.



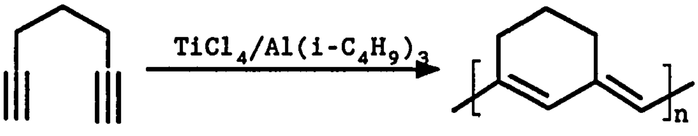
The product (exo-alkylidene)cyclobutene will decompose even at 38-40°C. This strain energy, however, can be released in the case of the silacyclobutene because of the longer Si-C bond length. Several examples of the stable (exo-alkylidene)silacyclobutenes[47] have been reported in the literature.

Recently Kusumoto and Hiyama[48] reported the polymerization of 3,3,5,5-tetramethyl-3,5-disila-1,6-heptadiyne 82 by using metathesis catalysts. The UV-visible λ_{max} of the polymer was only 263 nm. IR and ^1H NMR spectra but no ^{13}C and ^{29}Si NMR data were mentioned. The polymer structure was assigned to be a six-membered ring as shown in 83 based on the results reported for poly(1,6-heptadiyne)[22].



82 83

It must be noted that the structure assignment[22] of the poly(1,6-heptadiyne) 85 was mainly based on the stability of the six-membered ring. The reported ^{13}C NMR



84 85

(CP/MAS) spectrum of the poly(1,6-heptadiyne) is reproduced in Figure 32. Clearly the overlapping CH and C carbon signals at 130-140 ppm hamper a detailed structural analysis.

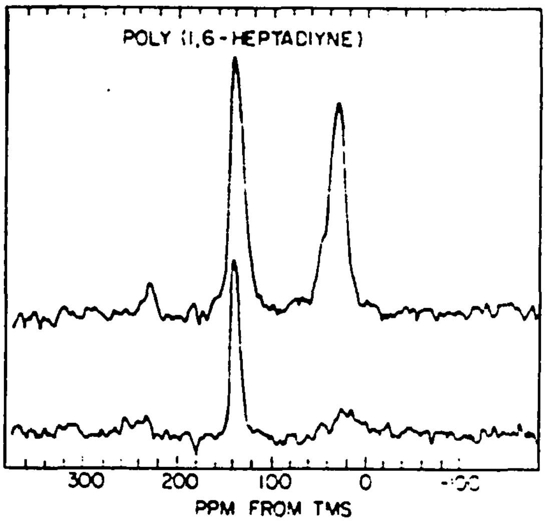
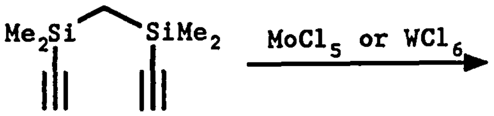


Figure 32. ^{13}C (CP/MAS) NMR spectrum of poly(1,6-heptadiyne): full spectrum (top), nonprotonated carbon-13 spectrum (bottom)

One way to approach this problem is to substitute the carbons at 3- and 5-positions of the 1,6-hepadiyne 84 by silicon atom, i.e., using diyne 82. Thus the carbon-13 signals in the vinyl region might be separated due to the perturbation of the silicon atoms. The other advantage in the polymerization of diyne 82 is associated with the ^{29}Si NMR which normally allows us to obtain more structural information. Polymerization of diyne 82 was reinvestigated by using $MoCl_5$ and WCl_6 catalysts. A red polymer was obtained in both cases with UV absorption λ_{max} about 440 nm (Figure 33).



82

Red polymer

86

Mw-11,330

PDI-3.9

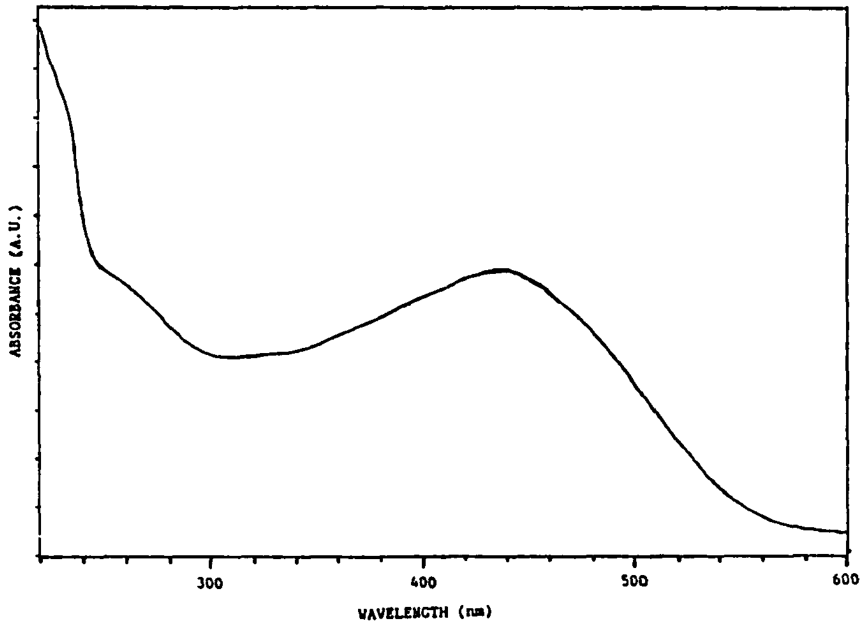


Figure 33. UV-visible spectrum of red polymer 86 (THF) by using WCl_6 catalyst

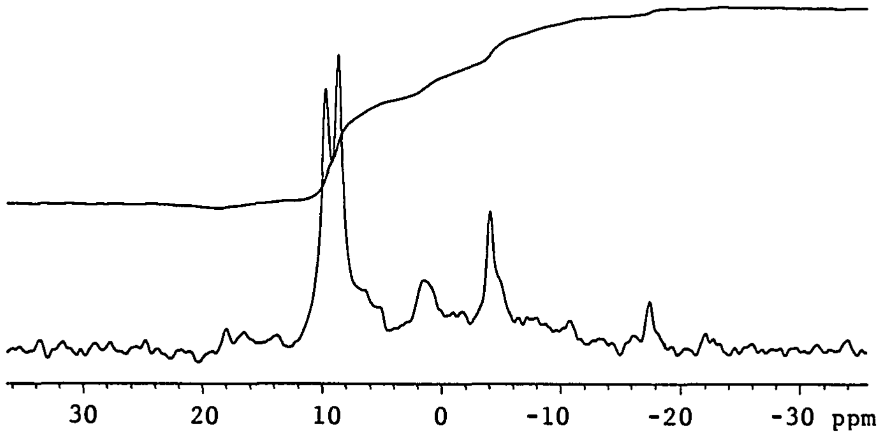


Figure 34. ^{29}Si{H} NMR spectrum (inverse-gated decoupling) of red polymer 86 from WCl$_6$

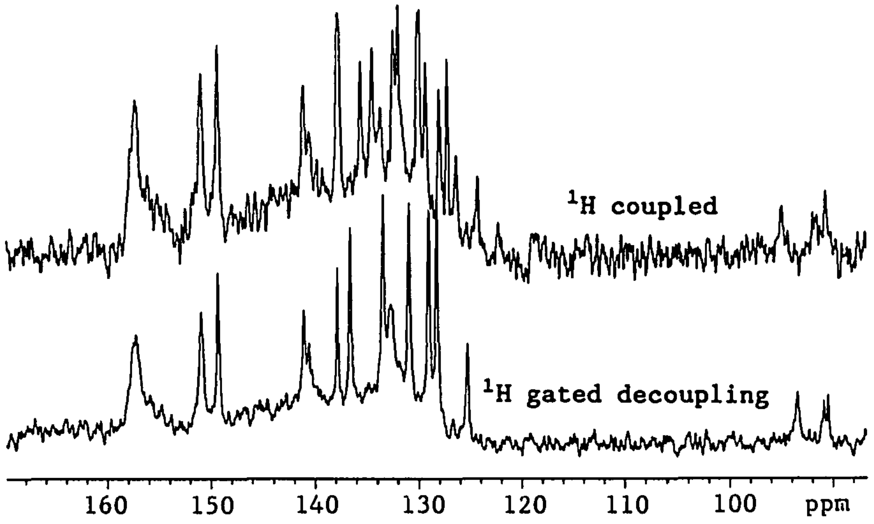


Figure 35. ^{13}C NMR spectrum of red polymer 86 from WCl$_6$: inverse-gated decoupling and proton-coupled spectrum (alkyl region not shown here)

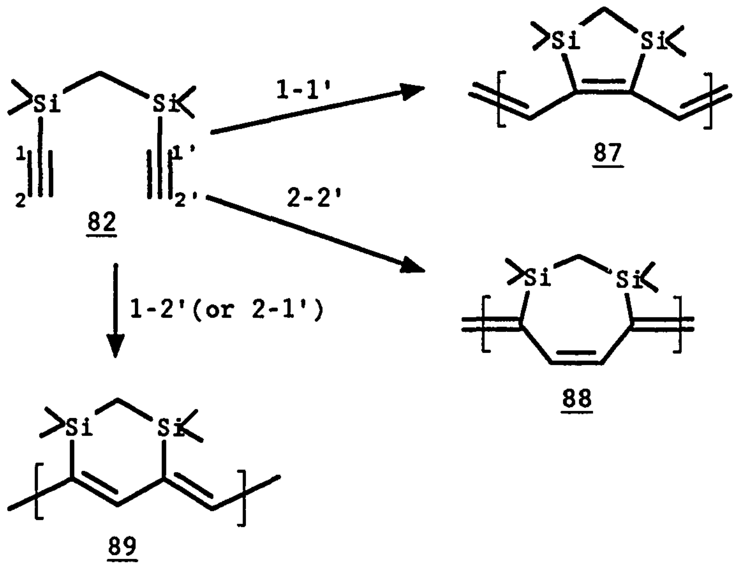
Quantitative ^{13}C and ^{29}Si NMR spectra of the red polymer <u>86</u> are shown in Figures 34 and 35. Both spectra are characterized by several sharp lines which are superimposed on a very broad background. This observation might suggest that the polymer is slightly crosslinked. The integration of ^{29}Si and ^{13}C signals are listed in Table 13. In the ^{13}C NMR spectrum, signals in the acetylenic carbon region are very weak, consisting only about 3.3%. Obviously the chemical structure for red polymer <u>86</u> is complicated.

Table 13. Integrations of ^{29}Si and ^{13}C in Figures 33 and 34.

Silicon-29 NMR		Carbon-13 NMR[a]	
δ shift range (ppm)	Integration(%)	δ shift range (ppm)	Integration(%)
20 ~ 13	2.6	170 ~ 159	7.1
13 ~ 7	41.2	159 ~ 155	10.4
7 ~ 3	8.6	155 ~ 152	2.5
3 ~ -2	16.9	152 ~ 148	10.5
-2 ~ -6	16.9	148 ~ 124	66.2
-6 ~ -15	10.0	90 ~ 95	3.3
-15 ~ -19	3.8		

[a] Only vinyl and acetylenic carbons are considered.

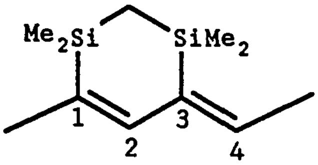
Katz et al.[50] has demonstrated by a ^{13}C-nutation NMR experiment that the new formed bond in the polymerization of an acetylene is a double bond (not a single bond!) when a metathesis catalyst is used. Keeping this point in the mind, all the possible ring structure units formed during the polymerization of diyne 82 will be the five-, six- and seven-membered ring as shown below.



The proton-coupled ^{13}C NMR experiment (Figure 35) clearly indicated that the resonance signals at 157 ppm, 151 ppm and 149 ppm are due to nonprotonated carbons. The resonance signal at 157 ppm in the ^{13}C NMR spectrum signifies the existence of an exo-cyclic double bond. Integration (Table 13) shows that this signal contributes 10.4% among all the vinyl and acetylenic carbons. If we assume that this signal at 157 ppm represents only one carbon in the repeating unit, then four times 10.4% comes to 41.6% which is equal to the integration area of the doublet signals (1:1 ratio) at 9.7 and 8.6 ppm in the

^{29}Si NMR (Figure 34). This result suggests the six-membered ring <u>89</u> is a building block for the polymer structure.

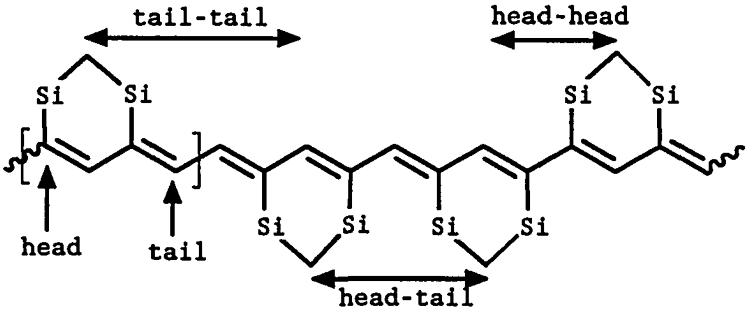
The two signals at ca. 150 ppm belong to nonprotonated carbons in a cycloalkene. The assignment for the carbon-13 signal can be made as below.



C-3: 157 ppm
C-1: 149.3 ppm
150.9 ppm

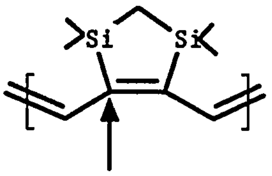
<u>89</u>

Since C-1 and C-3 are distinctly different, two silicon-29 signals with a slight difference in ppm are expected from the six-membered ring. The broad singlet at 157 ppm and the doublet at ca. 150 in the carbon-13 NMR can be explained when the head-tail and head-head sequences are considered. In the structural unit <u>89</u>, chemical shift of

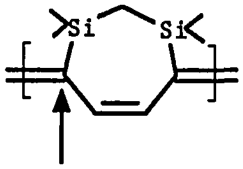


C-1 in the head-tail sequence is different from the one in the head-head sequence. However less effect will be expected on C-3 in the structural unit <u>89</u> when different sequences are considered. This is because of the existence of the C-4 carbon which acts like a buffer. So a slightly broadened signal (but not splitting) for C-3 was observed.

The possibility of a combination of five- and seven-membered ring structures 87 and 88 can be excluded based the observed broad singlet at 157 ppm and the doublet at ca. 150 ppm in the ^{13}C NMR. The five- and seven-membered ring structures are reproduced as below. The expected



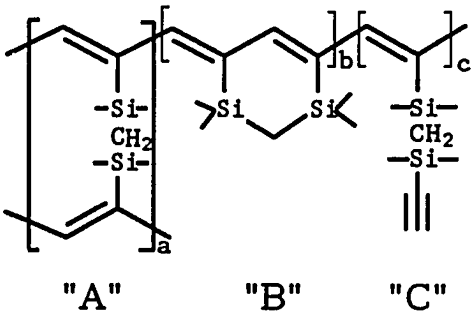
150 ppm in ^{13}C



157 ppm in ^{13}C

^{13}C chemical shift for nonprotonated vinyl carbons are indicated by the arrows. If the structure of the polymer 86 consists of the five- and seven-membered ring, the signal at 157 ppm should be affected more than signal at 150 ppm due to the different chain sequences. So the signal at 157 ppm should be more broad (or even split into two peaks) than the signal at 150 ppm. This is contradictory to what was observed in the ^{13}C NMR spectrum in Figure 35.

In summary the polymer structure of the red polymer can be expressed as follow. Here structural unit "A"



stands for all the unidentified units which include the branching or crosslinking units. From the ^{29}Si NMR spectrum in Figure 34, it is clearly seen that the major regular structure in the polymer is the six-membered ring structure unit "B". More accurate estimation of the content was hampered by the very broad line in the NMR spectrum. The content of dangling acetylene unit "C" is only about 6% based on the integration of the ^{13}C NMR spectrum.

Polymer 86 was an insulator. However, the conductivity could be increased to 3.4×10^{-3} σ/cm when the polymer was doped with AsF_5 under a vapor pressure of ca. 100 torr.

Physical Properties of Poly(diorganodiethynylsilane)

The thermal properties of poly(diorganodiethynylsilanes) were characterized by thermogravimetric analysis (TGA). As an example the TGA curve of poly(di-sec-butyldiethynylsilane) was illustrated in Figure 36. The decomposition commences at ca. 314°C, reaching a maximum rate at ca. 456°C. Different from the low char yields[51] reported for polyacetylene (25%) and poly(methylacetylene) (7%), char yield as high as 46% was obtained with poly(di-sec-butyldiethynylsilane). This high char yield is clearly related to the silicon atoms in the polymer backbone.

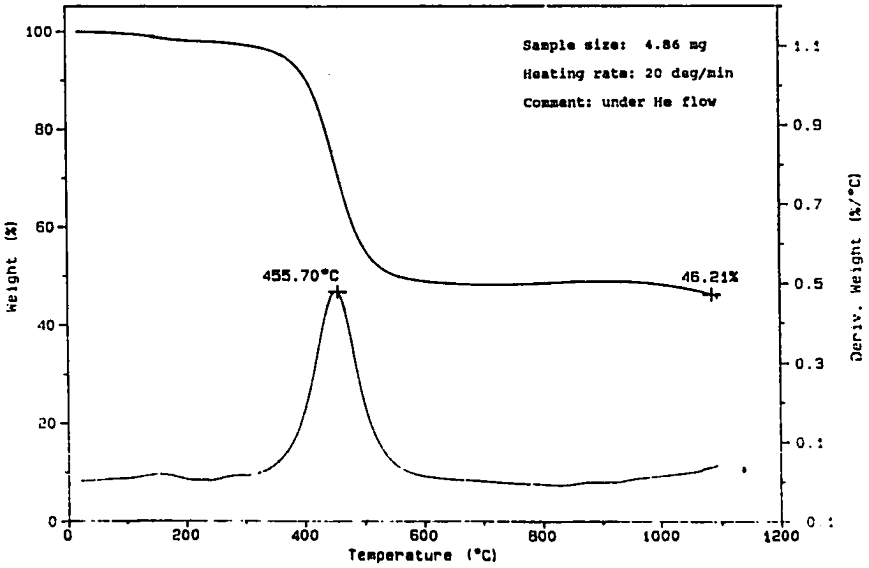
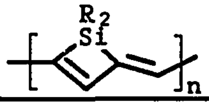


Figure 36. TGA curve of poly(di-sec-butyldiethynylsilane) at a heating rate of 20°C/min. under He flow

The volatile components produced during the pyrolysis were analyzed by an on-line mass spectrometer.

Below 500°C mainly C_4H_8 was observed accompanying with a trace amount of hydrogen and methane. After 500°C a significant amounts of hydrogen and methane were observed along with C_4H_8. Thermal properties of other polymers are summarized in Table 14.

Table 14. Thermal properties[a] of 

R	decomposition temp (°C)		char yield(%)
	on-set	maximum rate	
$i\text{-}C_3H_7$	329	478	53.2
$sec\text{-}C_4H_9$	314	456	46.2
$n\text{-}C_3H_7$	323	490	56.8
$n\text{-}C_4H_9$	300	500	48.2
$n\text{-}C_6H_{13}$	232	510	37.6
phenyl	300	572	65.1

[a] TGA were performed at a heating rate of 20°C/min up to 1100°C under He flow. Sample size 4~10mg.

Like most polymers with conjugated π-electron backbones, the poly(diethynylsilanes)[52] exhibit a strong ESR signal in either solid state or solution state. As an example, the ESR spectrum of the poly(diphenyldiethynylsilane) is shown in Figure 37. The sharp signal is due to a carbon radical. In Figure 37(a) the polymer had been precipitated out of methanol only once, and the EDX (energy dispersive X-ray) spectrum showed a significant amount of Mo atom. The Mo catalyst could be removed by performing several precipitations out of methanol. The ESR spectrum of the more pure polymer is shown in Figure 37(b). The significant decrease of the broad signal at ca. 3.40 KGauss indicates that this broad signal originates from the catalyst residue.

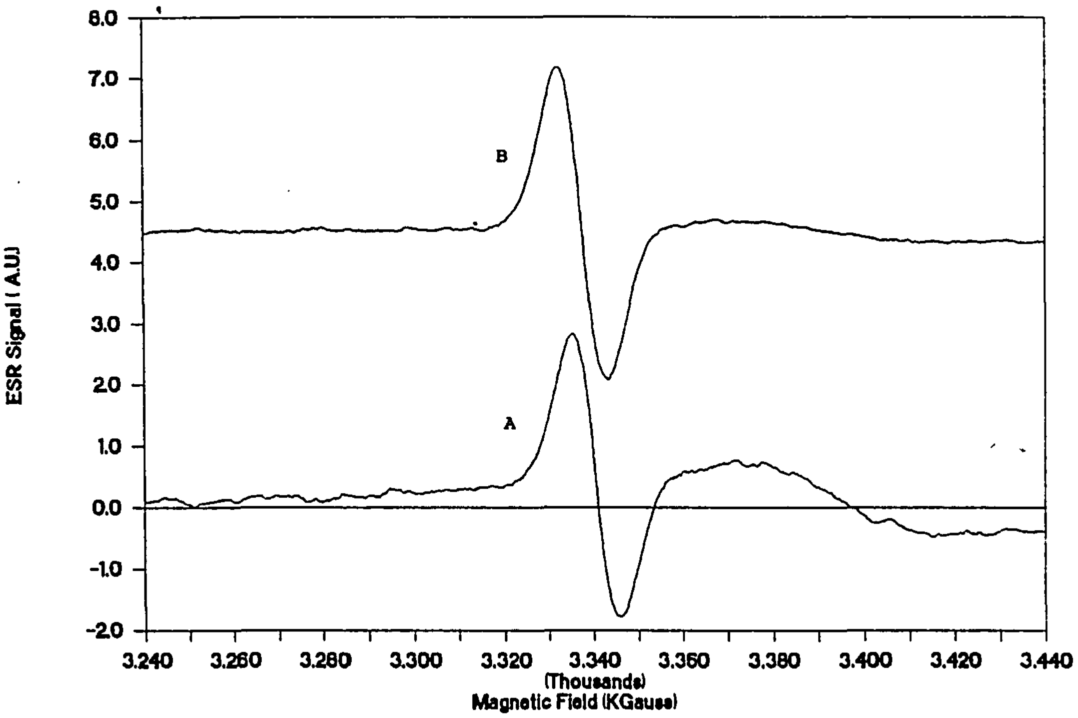


Figure 37. ESR spectra of the poly(diphenyldiethynylsilane) precipitated once (a) and three times (b) out of methanol

The poly(diorganodiethynylsilanes) are insulators at room temperature, having a conductivity of 10^{-8}-10^{-10} s/cm. A brief exposure to iodine atmosphere (doping), however, raises the conductivity up to 0.1 s/cm. As an example, the doping of poly(di-sec-butyldiethynylsilane) is shown in Figure 38.

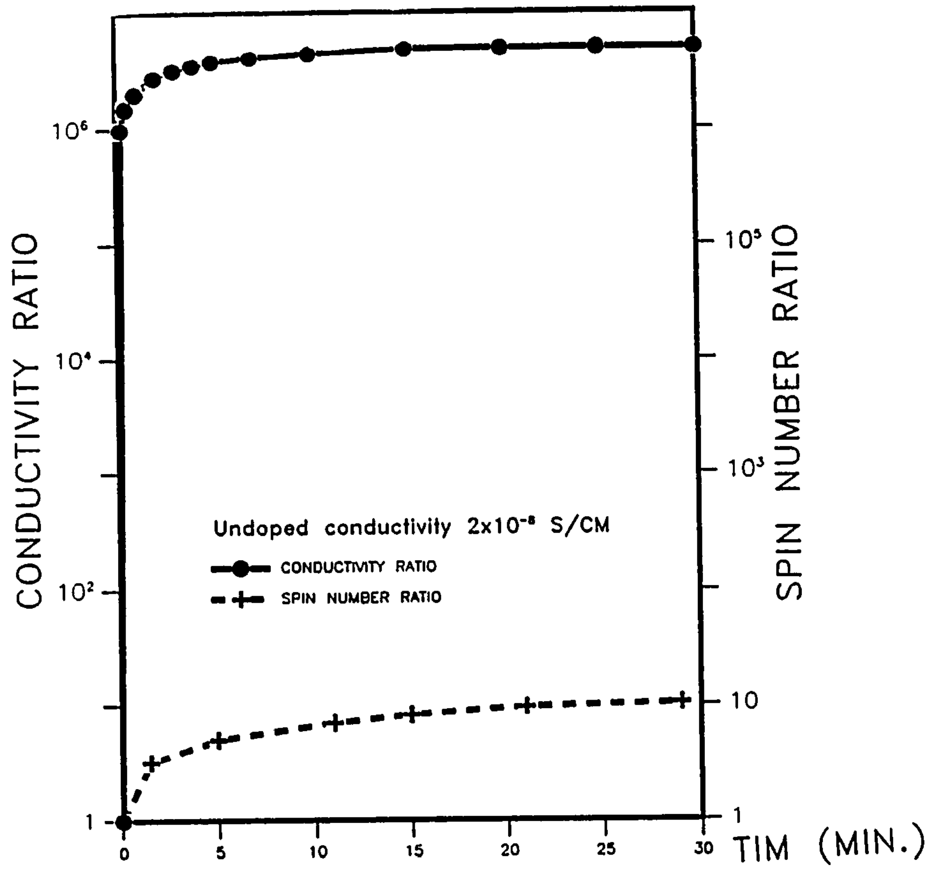
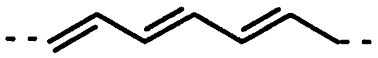


Figure 38. Electrical conductivity of poly(di-sec-butyldiethynylsilane) as a function of time when doped with a saturated I_2 atmosphere

The simplest polymer with a conjugated π-backbone, i.e., polyacetylene, can exist in two isomeric forms. The structures of the two forms (cis and trans) are

cis



trans

trans-Polyacetylene is unique among conducting polymers in that it possesses a degenerate ground state corresponding to the geometric forms shown in Figure 39.

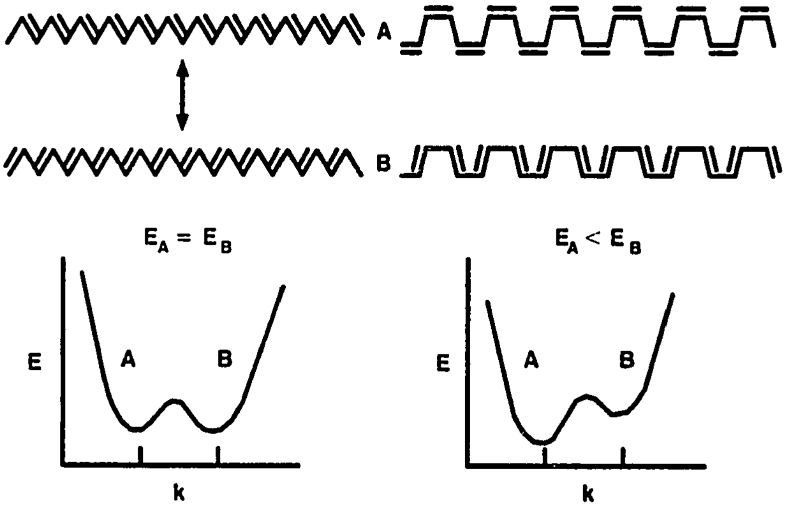
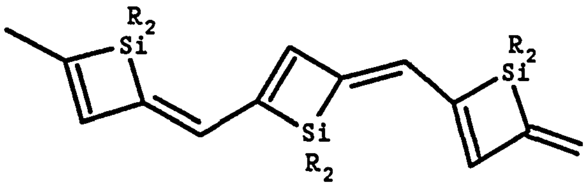


Figure 39. Energy diagram[53] for ground-state geometric isomers of trans- and cis-polyacetylene

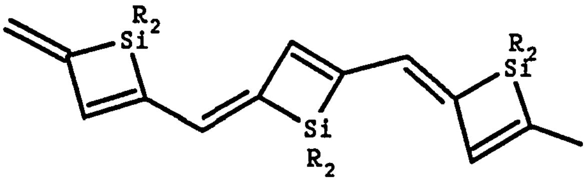
Ab initio calculations[54] have indicated that the trans-polyacetylene is more stable than the cis-polyacetylene by about 2 kcal $mole^{-1}$. In cis-polyacetylene, the cis-transoid form is lower in energy than the trans-cisoid form by 0.2 kcal/mol.

The two geometric isomers of the poly(diorganodiethynylsilane) are shown as follows:

A



B



Ab initio calculations[55] suggest that this π-conjugated polymer has a nearly-degenerate ground state. The energy difference between the two geometric isomers is within 0.05 eV. So the poly(diorganodiethynylsilane) can serve as the second example of the conducting polymer which has a degenerate ground state.

Nonlinear optical interaction is another interesting property which originates from a easily polarized π-electron cloud. When light passes through a material, the electromagnetic field associated with the light exerts a force on the π-electrons. As a result the electrons are slightly displaced in one direction, thus inducing a polarization. The polarization P in a bulk media which is induced by the incident electromagnetic field E can be expressed in a power series

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots,$$

where $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ are the first-, second- and third-order susceptibilities of the bulk media. In a glassy polymer (a nonordered media) the contribution of $\chi^{(2)}$ to nonlinear polarization is zero. Under this circumstance, $\chi^{(3)}$ is the first nonlinear term.

Important applications associated with a large $\chi^{(3)}$ include third harmonic generation (THG), optical bistability[56], phase conjugation[57] and their potential key role (logic operations) in optical computing[58]. This optical computer will process information $10^2 \sim 10^3$ times as fast as the electronic computers used today. In order to realize these technological applications, however, a material with a large $\chi^{(3)}$ value and a very fast response time is needed. The response time[59] is the time with which the material recovers following a control pulse so that it can respond to a second control pulse. Experimentally the response time can be obtained from a signal intensity decay curve by fitting the curve with an exponential function,

$$\Delta T(t) = A\ e^{-t/\tau}$$

here ΔT stands for transmittance change, A a constant and

τ the response time. Signal intensity as a function of decay time for polymer 53 from $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$ is shown in Figure 40.

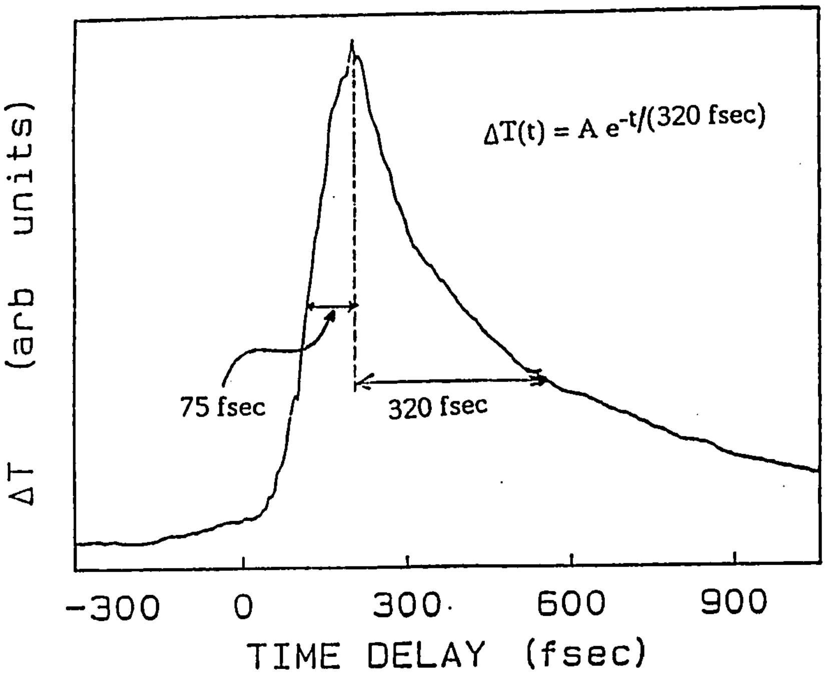


Figure 40. Time dependence of the photoinduced bleaching in polymer 53 from $(sec\text{-}Bu)_2Si(C{\equiv}CH)_2$

The reported $\chi^{(3)}$ values and response times for various compounds are summarized in Table 15. For inorganic materials such as ZnS, the nonlinearity ($\chi^{(3)}$) is large but the response time is slow. The organic materials are superior to the inorganic materials by offering not only a large nonlinearity (large $\chi^{(3)}$) and

Table 15. Typical $\chi^{(3)}$ values and response time

compound[a]	$\chi^{(3)}$ (e.s.u.)	responce time (second)	ref
ZnS(crystal)	10^{-5}	10^{-5}	60
Polydiacetylene (single crystal)	$9\times10^{-9} \sim 5\times10^{-10}$	$\sim6\times10^{-12}$	61
Polythiophene	10^{-9} (585 nm)[b]	12×10^{-12}	60
Polysilane	10^{-12}(360~1060 nm)	3×10^{-12}	60
Polyacetylene (oriented film)	$8.1\pm4\times10^{-9}$ (1064 nm)	----	62
Poly(p-phenylene vinylene) (oriented film)	4×10^{-10} (580 nm)	6×10^{-12}	63

[a] materials in amorphous state unless specified.
[b] wavelength at which the $\chi^{(3)}$ was measured.

also a fast response time. In terms of the optical switch, the response time is more important since it determines the speed an optical switch can operate.

The optical properties[64] of poly(diethynylsilane) have been examined. The measurements reveal that the polydiethynylsilane has a response time as short as ca. 300 femtosecond, i.e., 3×10^{-13} second. This is the fastest ever observed in the π-conjugated polymers, at least one order of magnitude faster than the other π-conjugated polymers. The third-order susceptibility $\chi^{(3)}$ of an amorphous polydiethynylsilane at 625 nm is 3×10^{-9} e.s.u., which is among the largest measured in organic conducting polymers.

CONCLUSIONS

Thermal polymerization of diphenyldiethynylsilane has been proved not to produce a diacetylene polymer which was reported by Luneva et al.[3], but to generate a red polyacetylene type polymer. The gaseous product formed during the reaction has been identified as acetylene, not hydrogen. ^{29}Si and ^{13}C NMR spectra have revealed that the chemical structure for the red polymer is complicated.

The diorganodiethynylsilane $R_2Si(C{\equiv}CH)_2$ has been found to polymerize in the presence of a metathesis catalyst, such as $MoCl_5$ and WCl_6, to lead to a soluble, air-stable, violet polymer. A regular structural unit has been developed during the polymerization. This repeating unit has been assigned to be a four-membered ring structure based on the NMR spectroscopic studies.

The type of alkyl group R in $R_2Si(C{\equiv}CH)_2$ is found to importantly affect the polymer structure when $MoCl_5$ is used as catalyst. If R is sterically hindered, such as sec-butyl and iso-propyl, a polymer backbone consisting mainly of one repeating unit is developed as characterized by one sharp peak in the ^{29}Si NMR spectra. When R is a n-alkyl, however, the product has three sharp signals in the ^{29}Si NMR spectra. This difference is also revealed in their UV-visible spectra.

Various physical properties of the polydiethynylsilane have been studied. The doped conductivity of the polymer is found to reach as high as 0.1 s/cm. The nonlinear optical properties, response time as high as 0.3 picosecond and $\chi^{(3)}$ value as large as $3\text{x}10^{-9}$ e.s.u., have been found to be among the best of all known conducting polymers.

The diethynylsilane $R_2Si(C\equiv CH)_2$ has two substituted acetylenes ajacent to each other. This structural feature allows the polydiethynylsilane combine the advantages of both polyacetylene and substituted polyacetylenes. The comparisons are summarized in Table 16.

Table 16. Comparison of properties of polydiethynylsilane with those of polyacetylene and substituted polyacetylene

substituted polyacetylene	pilyacetylene	polydiethynylsilane
Mw 10^5~10^6	Mw ~ 10^4	Mw ~ 10^4
colorless(or yellow)	black (powder)	violet or blue
soluble	insoluble	soluble
amorphous	crystalline	amorphous
air-stable	air-sensitive	air-stable
insulator	semiconductor	semiconductor
nonparamagnetic	paramagnetic	paramagnetic
$\chi^{(3)}$ negligible	$\chi^{(3)}$ 10^{-9} e.s.u.	$\chi^{(3)}$ 10^{-9} e.s.u.

EXPERIMENTAL

Most spectral data were obtained on the same instruments as that in Part 1 of this thesis. Ultraviolet absorption spectra were measured using a Perkin-Elmer Model 320 UV-VIS spectrometer. Solid state NMR spectra were obtained on a Bruker MSL 300 spectrometer.

Tungsten(VI) chloride, molybdenum(V) chloride, and methylmagnesium chloride were purchased from Aldrich. Tetraphenyltin was received from Alpha Products. Chlorosilanes and solvents were purified by distilling from CaH_2.

Preparation of Diphenyldiethynylsilane (1)

Diphenyldiethynylsilane was prepared as a white solid (100% pure by GC) by using the same procedure in Part 1 of this thesis.

Thermal polymerization of (1)

Diphenyldiethynylsilane (1.7 g) was placed in an argon-flushed, 5 mL one-neck, round-bottomed flask which was equipped with a magnetic stirrer. Heating this monomer at 155°C for 20 hours produced a minuscule amount (ca. 1.7%) of acetylene which was separated and analyzed by a on-line GCMS. The color of the liquid mixture changed to red during the initial heating and the mixture gradually became more and more viscous. Upon further heating at 200°C for 8 hours, the mixture was brick red and very viscous. The polymerization was stopped by cooling to room temperature. A clear, hard, dark-red solid was obtained, which was soluble in THF, benzene and $CHCl_3$. The polymer was precipitated out from THF solution with methanol, separated by centrifuge and dried in vacuum over 24 hours. Polymer yield was ca. 90%, with weight average molecular weight of Mw=19,000 from GPC. Prolonged heating at 200°C increased the molecular weight, but the product had a much lower solubilities. ^1H NMR of the polymer (CD_2Cl_2, 300 MHz) showed only one broad peak at 6-8ppm.

Thermal polymerization of (1) in diphenylether or xylene

A 10 mL one-necked, round-bottomed flask, equipped with a magnetic stirrer, was charged with 4 mL anhydrous diphenylether and 4 g diphenyldiethynylsilane. The air was replace by N_2 with freezing and thawing technique. Heating the solution at 150°C for 18 hours, and then 200°C for 20 hours produced a red viscous solution. A small amount of acetylene (ca. 1.7%) was observed by analyzing the volatile components in the gas phase by GCMS. The polymerization was stopped by cooling to room temperature. The red solution was dissolved in 20 mL THF, and precipitated out of methanol (100 mL). The precipitation was repeated one more time in order to completely remove diphenylether. Polymer yield was ca. 80%, with weight average molecular weight of Mw=15,000.

Thermal polymerization of (1) in presence of Cl_3C-CCl_3

A 5 mL round-bottomed, one-necked flask, equipped with a magnetic stirrer, was charged with 1.13 g of diphenyldiethynylsilane, 0.50 g of hexachloroethane and 1 mL of xylene. The air was replaced by N_2 with freezing and thawing technique. After heating the solution at 150°C for 18 hours, and then 200°C for 18 hours, no acetylene gas was liberated. GC analysis was performed by comparing the ratio of xylene to diphenyldiethynylsilane before and after the reaction. No change in this ratio was found. No any polymer was formed during the reaction based on GPC.

NaOD/D_2O decomposion of red polymer (4)

A 25 mL of oven-dried, nitrogen-flushed, one-necked flask equipped with a magnetic stirrer was charged with 8 mL of D_2O (99.7% deuterated). The flask was cooled by an ice-water bath. Sodium metal chips (1.05 g) was added portion by portion in a nitrogen atmosphere (in a glove bag filled with N_2). After the reaction quieted down, a colorless transparent solution was obtained. The solution concentration was ca. 12% by weight.

To another oven-dried, nitrogen-flushed, 10 mL one-necked flask which was equipped with a magnetic stirrer was added red polymer 4 (0.43 g) and 2 mL of anhydrous xylene. After the polymer was completely dissolved, 2 mL of the NaOD/D_2O solution was added through a syringe. The flask was pumped to 1.26 mmHg (or Torr) and then was closed in order to allow collection of the acetylene gas during the reaction. The mixture was heated to 55°C for 18 hours and then the flask was connected to a vacuum source with a U trap on line. After evacuated the U trap, the vacuum source was disconnected by closing a valve between the U trap and the vacuum source. The flask was cooled by a dry-ice bath and a valve between the U trap and the flask was opened, while the U trap was cooled by liquid nitrogen. The acetylene was frozen in the U trap. After all of the acetylene was frozen in the U trap, the valve between the U trap and the flask was closed. The U trap was allowed to warm up to room temperature. The pressure built up by the acetylene was measured through a on-line vacuum gauge. From this pressure and the volume of the U trap, ca. 1% of acetylene was found. The calculation was based on the assumption that the percentage of the acetylene in $Ph_2Si(C{\equiv}CH)_2$ was 100% and that all of the acetylene was liberated from the polymer.

Analyzing the gas by a on-line GCMS showed only deuterated acetylene and a trace amount of xylene, no deuterated butadiyne was found.

Preparation of dimethyldiethynylsilane (8)

Dimethyldichlorosilane (91 mL, 0.8 mol) was added dropwise during 0.5 hour to a solution of ethynylmagnesium chloride (1.65 mol in 1000 mL THF) prepared from acetylene and n-butylmagnesium chloride (1.65 mol) at ice temperature. The addition rate was slow enough to keep the temperature below 20°C. After addition the mixture was stirred at room temperature for overnight. The reaction mixture was cautiously poured into 500 mL (0.5 M) cold aqueous HCl solution. The organic layer was separated and washed two more times with dilute aqueous HCl solution. Finally the organic layer was dried over $NaSO_4$. Product with bp 83-88°C was collected via fractional distillation through a 60 cm column packed with glass helices. After thirty washings with dilute aqueous HCl solution, 70 grams of dimethyldiethynylsilane (96% pure by GC, 78% yield) was obtained.

The residue was further distilled under vacuum to give 8 grams of a mixture containing 8 (30%), dimer 9 (60%) and trimer $HC{\equiv}C{-}SiMe_2{-}C{\equiv}C{-}SiMe_2{-}C{\equiv}C{-}SiMe_2{-}C{\equiv}CH$ (10%). Dimer 9 (3.0 g, 99% pure by GC, mp 57.5-58°C) was crystallized from the mixture and had the following spectral properties. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.353 ppm (s, 6 H); 2.453 ppm (s, 1 H). Mass spectrum 190 (1) M^+; 189 (2) M^+-1; 178 (1); 177 (8); 176 (20); 175 (100) M^+-Me; 102 (18); 53 (50).

Thermal polymerization of (8) and (9)

A 10 mL nitrogen-flushed sealed tube equipped with a valve was charged with 1 g of compound 8 (or 9). The bottom of the tube was heated at 150°C for 18 hours and then 200°C for 12 hours in an silicon oil bath. The product 10 (or 11) was a red solid which was hard, brittle and not soluble in THF. Analysis of the gas phase indicated that a small amount of acetylene was formed during the heating. The ^{29}Si and ^{13}C NMR (CPMAS) spectra of the red solid were shown in Figures 6, 7 and 8.

Preparation of $Ph_2Si(C{\equiv}CD)_2$

In a 25 mL one-necked, round-bottomed, nitrogen-flushed flask equipped with a magnetic stirrer, $Ph_2Si(C{\equiv}CH)_2$ (2.628 g, 11.3 mmol) was dissolved into 6 mL THF. Methylmagnesium chloride (23 mmol, 3 M solution in THF, 7.54 ml) was added dropwise through a syringe into the mixture at ice temperature. Then the solution was stirred at 50°C for 3 hours.

In another 25 ml one-necked, round-bottomed, nitrogen-flushed flask, 2 mL deuterium chloride (37 wt % solution in D_2O, 99 atom % D) was further diluted with 2 mL D_2O. To the deuterium chloride solution the $Ph_2Si(C{\equiv}CMgCl)_2$ solution prepared above was added slowly dropwise through a syringe under a nitrogen atmosphere at ice temperature. After addition, the mixture was stirred at 0°C for 20 minutes. The organic layer was separated and washed by H_2O. Following removal of solvent the product was collected at 136-137°C/1 mmHg (95 % yield) as a colorless solid with mp 44-45°C. The ^1H NMR ($CDCl_3$, 300 MHz) showed only phenyl protons at δ 7.424 (m, 3 H) and 7.765 (m, 2 H); no acetylenic proton was found.

Thermal polymerization of $Ph_2Si(C{\equiv}CD)_2$

Conditions for thermal polymerization were the same as in the preparation of red polymer 4.

Synthesis of $(C_6D_5)_2SiCl_2$ (15)

To a 250 mL round-bottomed, three-necked, nitrogen-flushed flask which was equipped with a magnetic stirrer, a condenser, and a pressure-equallizing addition funnel, was added 110 mL of diethyl ether and magnesium turnings 6.7 g (0.25 mol). Deuterated bromobenzene 40 g (0.247 mol, 26 mL) was added dropwise through the addition funnel while the reaction mixture was stirred vigorously. The addition rate was slow enough to maintain gentle reflux. After the addition was complete, Stirring was continued for another 10 minutes.

To another 500 ml nitrogen-flushed flask, equipped with a magnetic stirrer and a condenser, was added 250 mL of hexane and 13.7 mL $SiCl_4$ (0.12 mol). The Grignard solution prepared above was slowly added dropwise into the $SiCl_4$ solution while it was stirred vigorously. After addition the mixture was stirred at room temperature for overnight. The salts which were generated during the reaction were removed by passing through a sintered glass filter. The organic solution was concentrated to ca. 70 ml volume. GCMS analysis of the crude product showed 92.5% of $(C_6D_5)_2SiCl_2$, 3.8% of $C_6D_5SiCl_3$, 3.7% Of $(C_6D_5)_3SiCl$ in the solution. The solution was used in the next step without further purification.

Synthesis of $(C_6D_5)_2Si(C{\equiv}CH)_2$ (16)

The crude product $(C_6D_5)_2SiCl_2$ prepared above was added dropwise during 20 minutes into a solution of ethynylmagnesium chloride (0.25 mol in 250 ml THF) at -78°C. After 20 minutes stirring, the mixture was gradually warmed to room temperature for overnight. Then the reaction mixture was poured portion by portion into 200 mL cold dilute HCl aqueous solution. The organic layer was separated and washed one more time with dilute HCl aqueous solution. Finally the organic layer was dried over anhydrous Na_2SO_4. After removing most of the solvent on a rotatory evaporator, the product was collected at 136-137°C/1 mmHg as a colorless solid (mp 43.5-44.0°C) with 77% overall yield. ^1H NMR ($CDCl_3$, 300 MHz) of the product showed only one singlet at δ 2.74 ppm, no phenyl proton was observed. Mass spectrum 243 (17); 242 (78) M^+; 241 (77) M^+-H; 240 (100); 187 (16);

160 (48) $M^+-C_6D_5$; 159 (24); 158 (15); 135 (23); 134 (41); 133 (33); 110 (19); 107 (16); 106 (18); 82 (21); 78 (16); 77 (15).

Thermal polymerization of $(C_6D_5)_2Si(C{\equiv}CH)_2$

A half gram of $(C_6D_5)_2Si(C{\equiv}CH)_2$ was thermally polymerized under the same condition as for $Ph_2Si(C{\equiv}CH)_2$.

The product was dissolved in methylene chloride and then precipitated out by adding the solution dropwise into methanol. The precipitation was repeated twice in order to completely remove the low molecular weight product. The polymer was dried under vacuum 0.2 mmHg for overnight. The ^1H NMR (CD_2Cl_2, 300 MHz) spectrum (Figure 9) was acquired by using a recycle time of 15 seconds to assure complete relaxation.

Bromination of the red polymer (4)

In a culture tube equipped with a magnetic stirrer, red polymer 4 (0.5 g) was mixed with excess bromine (2 ml) and chloroform (2 ml). The tube was closed and was heated to 80°C for 4 hours. GCMS analysis indicated that bromobenzene (ca. 5% in the product solution) was the only volatile compound formed in the reaction.

Polymerization of $Ph_2Si(C{\equiv}CH)_2$ using carbon tetrachloride as solvent and $Mo(CO)_6$-$h\nu$ as catalyst

To a 25 ml quartz tube equipped with a magnetic stirrer was added $Mo(CO)_6$ (0.03 g, 0.1 mmol) and 6 mL of CCl_4 under a N_2 atmosphere. The solution was irradiated with a UV light at room temperature for 30 minutes before use. The color of the solution was yellow orange. The monomer $Ph_2Si(C{\equiv}CH)_2$ (1.163 g, 5 mmol) was dissolved in 1 mL of CCl_4 and was injected into the tube through a syringe. After heating ca. 5 minutes at 80°C, the color of the solution turned into dark brown or red. The solution was then stirred at 80°C for 24 hours. The polymer was precipitated by adding to a large amount of methanol (25 mL). The precipitated polymer was separated by centrifugation and dried to a constant weight under vacuum (yield ca. 10%). The molecular weight of the polymer was 10,000 by GPC. UV-visible spectra of the polymer showed a pronounced shoulder at ca. 440 nm and a long tail up to 700 nm. ^1H and ^{13}C NMR spectra of the polymer were the same as those for the violet polymer from $MoCl_5$.

Polymerization of $Ph_2Si(C{\equiv}CH)_2$ in the presence of catalyst $MoCl_5$

A solution of $Ph_2Si(C{\equiv}CH)_2$ (2 g) in 25 mL of anhydrous benzene was placed in an argon-flushed, 50 mL, round-bottomed flask which was equipped with a magnetic stirrer and capped with a rubber septum. The solution was deoxygenated by freezing to -78°C, evacuating, refilling with argon and thawing. This procedure was repeated at least twice in order to remove all trace of oxygen. Catalyst, $MoCl_5$ (ca. 50 mg), was added into the flask in a glove box under an argon atmosphere. The solution was heated to 60°C and a violet color was gradually developed in about an hour. After stirring at 60°C for 15 hours, the polymerization was quenched by dropwise addition of the reaction mixture to 150 mL of deoxygenated methanol. The precipitated polymer was separated by filtration and dried to a constant weight (under vacuum for overnight). The polymer yield was 54% (1.08 g brown solid). The polymer was soluble in common organic solvent, e.g., benzene, toluene, chloroform, methylene chloride, THF, and partially soluble in hexane.

GPC of the polymer product showed the weight average molecular weight (Mw) was 105,308 with polydispersity (Mw/Mn) of 1.91. The polymer had the following spectral properties. UV-visible absorption in THF: λ_{max} = 550 and 580 (sh) nm. IR (KBr pellet) showed only very weak acetylenic absorption at 2035 and 3269 cm^{-1}. Proton decoupled ^{13}C NMR ($CDCl_3$, 75.429 MHz) spectrum (Figure 13) showed three broad peaks at 135, 130 and 128 ppm overlapping each other. ^{29}Si NMR ($CDCl_3$, 59.591 MHz) (Figure 11) -10 to -20 ppm (28.8%), -20 to -26 ppm (35.6%), -26 to 42 ppm (35.6%).

Polymerization of $Ph_2Si(C{\equiv}CH)_2$ using WCl_6 as catalyst at 60°C

A solution of $Ph_2Si(C{\equiv}CH)_2$ (2 g) in 50 mL of anhydrous toluene was placed in an oven-dried, 100 mL, round-bottomed flask which was equipped with a magnetic stirrer and capped with a rubber septum. The solution was deoxygenated by freezing to -78°C, evacuating, refilling with argon and thawing. This procedure was repeated twice in order to remove all trace of oxygen. Catalyst WCl_6 (ca. 100 mg) was added in a glove bag under an argon atmosphere. The color of the solution became violet after it was heated to 60°C for two hours. The solution was then stirred at this temperature overnight (ca. 15 hours). The polymer was precipitated by dropwise addition of the solution to 150 mL deoxygenated methanol.

After separation by filtration and drying to a constant weight (under vacuum overnight), a dark brown polymer powder (1.19 g, 60% yield) was obtained. Most of the polymer was not soluble in THF and benzene, but suspended in solution in the form of very fine particles. The polymer had the following spectral properties.
UV-visible absorption in THF λ_{max} = 540nm. ^{29}Si NMR ($CDCl_3$, 59.591 MHz) -10 to -20 ppm (25.8%), -20 to -26 ppm (36.2%), -26 to -42 ppm (38.0%).

Polymerization of $Ph_2Si(C{\equiv}CH)_2$ using WCl_6 as catalyst at room temperature

In order to decrease the degree of crosslinking in the polymer, higher dilution and lower temperature was used in this experiment. A solution of $Ph_2Si(C{\equiv}CH)_2$ (1.13 g) in 50 mL anhydrous toluene was placed in an oven-dried, round-bottomed, 100 mL flask which was equipped with a magnetic stirrer and capped with a rubber septum. The solution was deoxygenated by freezing to -78°C, evacuating to 1 torr, refilling with argon and thawing. This procedure was repeated twice. Catalyst WCl_6 (100 mg) was added in a glove bag under an argon atmosphere. The color of the solution became red after it was stirred at room temperature for two hours. The solution was then stirred for overnight (ca. 15 hours). Following precipitation by addition to 150 mL deoxygenated methanol and separation by filtration, a dark brown polymer powder (0.57 g, 51% yield) was obtained. The polymer had the following spectral properties. GPC: Mw = 32,756, polydispersity index 3.9. UV-visible absorption in THF λ_{max} 480 nm. ^{29}Si NMR ($CDCl_3$, 59.591 MHz) -10 to -20 ppm (18.7%), -20 to -26 ppm (47.5%), -26 to -42 ppm (33.7%).

Synthesis of di(sec-butyl)dichlorosilane

To a 1000 mL oven-dried, round-bottomed flask equipped with a mechanical stirring and a pressure-equalizing addition funnel was added 250 mL anhydrous hexane and 45 mL silicon tetrachloride (0.392 mol) under a N_2 atmosphere. The solution was cooled to -78°C by a dry-ice bath. Under vigorous stirring, 0.784 mole of sec-butyllithium was added dropwise into the hexane solution during three hours. After addition the mixture was stirred at -78°C for an hour, then was gradually warmed to room temperature for overnight. The salt was removed by passing through a sintered glass filter under a N_2 atmosphere. The solvent was separated by fractional distillation through a 25 cm column packed with glass helices. Di(sec-butyl)dichlorosilane was obtained at 58-60°C/2mmHg in 58% (54 grams) yield. The product was 90% pure by GC, and was used in the next step without further purification. Mass spectrum of the product: 216 (0.25) $M^{+}+4$; 215 (0.18); 214 (1.19) $M^{+}+2$; 213 (0.32); 212 (1.73) M^{+}; 179 (0.26); 177 (0.66); 159 (1.17); 158 (0.75); 157 (6.27); 155 (9.59) $M^{+}-C_4H_9$; 153 (0.14); 143 (0.24); 141 (0.58); 139 (0.48); 137 (0.28); 135 (0.52); 131 (1.21); 130 (0.77); 129 (6.55); 128 (2.40); 127 (10.46); 126 (2.62); 125 (1.66); 123 (0.44); 121 (0.76); 120 (0.35); 119 (1.60); 118 (0.58); 117 (1.98); 116 (1.98); 115 (25.83); 113 (39.19); 107 (0.50); 106 (0.22); 105 (1.20); 103 (1.54); 102 (1.09); 101 (6.89); 100 (4); 99 (10.32); 98 (5.05); 95 (0.63); 94 (0.46); 93 (1.75); 92 (1.01); 91 (1.07); 90 (0.40); 89 (0.32); 83 (0.35); 81 (1.16); 80 (0.65); 79 (3.27); 78 (1.24); 77 (0.40); 69 (0.23); 67 (1.24); 66 (0.84); 65 (6.64); 64 (1.60); 63 (13.71); 58 (1.04); 57 (23.05); 56 (100); 53 (44); 51 (1.67); 50 (0.83); 45 (0.32); 43 (2.02); 42 (4.91); 41 (53.36).

Synthesis of di(sec-butyl)diethynylsilane (47)

A solution of 0.51 mole of ethynylmagnesium chloride in 500 mL of THF was cooled to -78°C by a dry ice bath.

Di(sec-butyl)dichlorosilane was added over 20 minutes while the ethynylmagnesium chloride suspension was vigorously stirred. After an additional one hour of stirring, the cooling bath was removed and the temperature was gradually warmed to room temperature for overnight. The reaction mixture was cautiously poured into 200 mL of cold dilute HCl aqueous solution (0.5 M). After vigorously shaking, the organic layer was separated and was further washed twice by dilute HCl aqueous solution. The organic layer was dried over Na_2SO_4. Fractional distillation through a 25 cm column which was packed with glass helices gave di(sec-butyl)diethynylsilane as a colorless liquid, bp 59-60°C/1.6mmHg, in 81% yield. The product was 96% pure. Another 4% unknown impurity, which had a similar boiling point as the product and contained neither acetylenic group nor silicon (confirmed by GC-MS and IR), came from di(sec-butyl)dichlorosilane preparation step. This product <u>47</u> was directly used in the polymerization studies without further purification. The product had the following spectral properties. Mass spectrum 192 (4.6) M^+; 136 (16.3) $M^+-C_4H_8$; 135 (52.9) $M^+-C_4H_9$; 121 (7); 109 (21); 108 (10.5); 107 (35.7); 105(10.7); 95 (15); 94 (15.6); 93 (100); 81 (9); 80 (10); 79 (72.8); 57 (13); 56 (17.7).

^1H NMR ($CDCl_3$, 300 MHz) δ 2.46 ppm (t, 1 H); 1.72 ppm (m, 1 H); 1.33 ppm (m, 1 H); 1.09 (d, J=7.5 Hz, 3 H); 1.00 ppm (t, J=7.2 Hz, 3 H); 0.86 ppm (m, 1 H). ^{13}C NMR ($CDCl_3$, 75.429 MHz, ^1H gated decoupling) δ 95.66 ppm (t, ca.3.28 Hz difference between two adjacent peaks, 1 C); 83.97 ppm (t, ca. 4.1 Hz between two adjacent peaks, 1 C); 24.65 ppm (d, 1.056 Hz difference, 1 C); 19.22 ppm (d, 0.603 Hz difference, 1 C); 13.58 ppm (d, 1.056 Hz difference, 1 C); 13.31 ppm (d, 0.981 Hz difference, 1 C). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ 25.527 and 25.580 ppm.

Anal. Calcd for $C_{10}H_{20}Si$: C, 74.92; H, 10.48.
Found: C, 74.43; H, 10.65.

<u>Synthesis of di(iso-propyl)diethynylsilane (48)</u>

A solution of 0.28 mole of ethynylmagnesium chloride, which was prepared in 290 mL of anhydrous THF, was cooled to -78°C. Di(iso-propyl)dichlorosilane (25 g, 0.135 mole, from Petrarch System Inc.) was added dropwise into the HC≡CMgCl suspension over 15 minutes while a vigorous stirring was maintained. After an additional one hour stirring, the cooling bath was removed and the temperature was allowed to rise to room temperature gradually. After stirring overnight, the reaction mixture was cautiously poured into 150 mL of cold dilute HCl aqueous solution (0.5 M). After vigorously shaking in a separation funnel, the organic layer was separated and was further washed twice by dilute HCl aqueous solution. Finally the organic layer was dried over Na_2SO_4. Fractional distillation through a 25 cm column which was packed with glass helices afforded 17.4 g colorless liquid (purity 99.5%, separation yield 76.8%). at 70-73°C/20mmHg. The product had the following spectral properties. Mass spectrum 164 (10) M^+; 121 (50) $M^+-C_3H_7$; 93 (100); 79 (15); 53 (32). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 1 H); 1.13-1.03 (m, 7 H). ^{13}C NMR ($CDCl_3$, 75.429 MHz, ^1H gated decoupling) δ 95.32 (C≡CH, 1 C); 82.93 (Si-C≡, 1 C); 17.10 (CH_3, 2 C); 11.57 (CH, 1 C). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ -22.93 ppm (singlet). Anal. Calcd for $C_{10}H_{16}Si$: C, 73.09; H, 9.81.

Found: C, 73.11; H, 9.54.

Polymerization of (sec-Bu)$_2$Si(C≡CH)$_2$ using $MoCl_5$ as catalyst

In a 50 mL oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar, 2 mL (1.76 g) of (sec-Bu)$_2$Si(C≡CH)$_2$ was dissolved in 25 mL anhydrous benzene. The solution was deoxygenated by freezing to

-78°C, evacuating to less than 1 torr, refilling with argon and thawing. This procedure was repeated twice in order to completely remove all trace of oxygen. Catalyst $MoCl_5$ (ca. 50 mg) was added to the monomer solution in a glove bag under an argon atmosphere. The flask was capped with a rubber septum which was connected to a balloon full of argon in order to maintain a positive argon atmosphere pressure. The color of the solution changed to violet after it was heated at 60°C for 30 minutes. The solution was then stirred at this temperature overnight (ca. 16 hours). The polymer was precipitated out by dropwise addition of the violet solution into 160 ml of deoxygenated methanol. After separated by filtration and dried on a vacuum line to a constant weight, a dark brown polymer powder was obtained in 45.5% yield. The polymer was readily soluble in THF, cyclohexane, benzene, chloroform. This polymer could be easily cast into a flexible film of golden luster from a chloroform solution. The film would gradually lose its flexibility upon exposure to air (oxygen) for a few weeks. The polymer had the following spectral properties. GPC: Mw = 63,656, polydispersity index 1.81. UV-visible absorption in THF: λ_{max} 565 nm, 600(sh) nm. ^{13}C NMR ($CDCl_3$, 75.429 MHz) 13.355 (s, peak width at half height ($W_{1/2}$) 1.3 ppm, 2 CH_3), 19.119 (s, $W_{1/2}$ 1.9 ppm, CH), 24.968 (s, $W_{1/2}$ 1.6 ppm, CH_2), 86 (s, $W_{1/2}$ 2.4 ppm), 96 (s.b, $W_{1/2}$ 1.8 ppm), 126-162 (very broad, multiplet peaks overlapping). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) 10 ~ 0 ppm (26%), 0 ~ -5 ppm (42%), -5 ~ -15 ppm (32%).

Polymerization of (sec-Bu)$_2$Si(C≡CH)$_2$ using WCl_6 as catalyst

In a 100 mL oven-dried, round-bottomed flask equipped with a magnetic stirring bar, 2 mL (1.76 g) of (sec-Bu)$_2$Si(C≡CH)$_2$ was dissolved into 50 mL of anhydrous toluene. After the solution was deoxygenated by the same procedure as last experiment, 120 mg of catalyst WCl_6 was added to the solution in a glove box under an argon atmosphere. The solution changed from yellow brown to violet after it was heated at 52°C for ca. five hours. After continuously heating overnight (total 16 hours), the polymerization was stopped by dropwise addition of the polymer solution into 200 mL of deoxygenated methanol. After separation by filtration and drying on a vacuum line to a constant weight, a brown polymer powder was obtained (0.8 g, 45.5% yield). The polymer had the following spectral properties. UV-visible absorption in THF: λ_{max} 550 nm, 600(sh) nm. GPC: Mw = 66,335, PDI=2.45. ^{13}C NMR spectrum was similar to the polymer from $MoCl_5$ catalyst. ^{29}Si NMR ($CDCl_3$, 59.591 MHz) 10 ~ 0 ppm (22.7%), 0 ~ -5 ppm (58.8%), -5 ~ -15 ppm (18.5%).

Polymerization of $(iso\text{-}Pr)_2Si(C{\equiv}CH)_2$ using $MoCl_5$ as catalyst

In a 50 mL oven-dried, round-bottom flask which was equipped with a magnetic stirring bar, 1 mL (ca. 0.87 g) of $(iso\text{-}Pr)_2Si(C{\equiv}CH)_2$ was dissolved in 25 mL of anhydrous benzene. The solution was deoxygenated by freezing to -78°C, evacuating to less than 1 torr, refilling with argon and thawing. This procedure was repeated three times to ensure the complete removal of trace oxygen. Catalyst $MoCl_5$ (ca. 50 mg) was added into the monomer solution in a glove box in an argon atmosphere. The flask was fitted with a condenser and capped with a rubber septum. An argon balloon was connected to the reaction vessel to maintain a positive argon pressure. After heating the solution at 60°C for 16 hours, a violet solution was obtained. The polymer solution was added dropwise in 150 mL deoxygenated methanol. After separation by filtration and drying on a vacuum line, a brown polymer powder was collected (0.5 g, yield 57%). The polymer had the following spectral properties.

UV-visible absorption λ_{max} 550 nm, 600(sh) nm in THF; λ_{max} 550 nm, 600(sh) nm in hexane. GPC: Mw = 32,255, PDI = 4.09. ^{13}C NMR ($CDCl_3$, 75.429 MHz) 12.02 (CH, 1 C, $W_{1/2}$ 1.8 ppm), 18.24 (CH_3, 2 C, $W_{1/2}$ 1.2 ppm), 85 ppm (C, $W_{1/2}$ 2.4 ppm), 96 ppm (CH, $W_{1/2}$ 1.6), 130-160 ppm (very broad, multiplet peaks overlapping). ^{29}Si NMR of solid state (CP/MAS) is shown in Figure 19(a).

Polymerization of (iso-Pr)$_2$Si(C≡CH)$_2$ using WCl_6 as catalyst

In a 100 mL oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar, 2 mL (1.74 g) of diisopropyldiethynylsilane was dissolved in 50 mL of anhydrous toluene. After the solution was deoxygenated by freezing and thawing techniques, 120 mg of catalyst WCl_6 was added in the solution in a glove bag under an argon atmosphere. After the solution was heated to 60°C overnight (ca. 15 hours), a violet solution was obtained. The violet solution was added dropwise at room temperature into ca. 200 mL of deoxygenated methanol. A brown polymer powder (0.84 g, 48% yield) was collected after separation by filtration and drying on a vacuum line to a constant weight. The polymer had the following spectral properties. UV-visible absorption in THF: λ_{max}

546 nm, 595(sh) nm. GPC: Mw = 10,231; polydispersity index 5.52. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 11.5 ppm (CH, 2 C, $W_{1/2}$ 1.4 ppm); 18.5 ppm (CH_3, 4 C, $W_{1/2}$ 1.5 ppm); 85.2 ppm (s, $W_{1/2}$ 1.8 ppm, 0.362 C); 96.0 ppm (s, $W_{1/2}$ 2.2 ppm, 0.362 C); 128-154 ppm (broad, multiplet peaks overlapping, 2.824 C); 154-158 (s, $W_{1/2}$ 2.6 ppm, 0.452 C).

Preparation of phenyldimethylethynylsilane (56)

In a 50 mL oven-dried, round-bottomed, three-necked flask which was equipped with a magnetic stirring bar, a gas inlet and an outlet, 22 mmol of $HC\equiv CMgCl$ was prepared from acetylene and methylmagnesium chloride (22 mmol) in 25 mL anhydrous THF. The suspension of $HC\equiv CMgCl$ was cooled to -78°C after it was prepared. Phenyldimethylchlorosilane (3.5 mL, 21.16 mmol, from Petrarch Systems) was added dropwise through a syringe. After addition, the mixture was stirred at -78°C for an hour, then at room temperature for two hours. The reaction mixture was cooled down to 0°C by an ice-water bath, and then ca. 7 mL dilute ice-cold HCl aqueous solution (ca. 0.2 M concentration) was added. After stirring for a few minutes, the organic layer was separated. GC-MS of the organic layer showed that phenyldimethylethynylsilane was a single product. The solvent was removed through distillation. A colorless liquid (3.2 g, 98% pure by GC, yield 93%) was collected at 58°C/2-4 torr. The product had the following spectral properties. Mass spectrum 160 (21.7) M^+; 146 (13); 145 (100) M^+-Me; 53 (30.4). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.639 (m, 2 H); 7.396 (m, 3 H); 2.522 (s, 1 H); 0.455 (s, 6 H). ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ -1.18 ($Si-CH_3$); 88.14 (Si-C≡); 94.82 (≡CH); 127.78, 129.63, 133.65, 136.30 (phenyl carbons). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ -21.07 ppm.

Synthesis of compound (57) via palladium catalyzed coupling between phenyldimethylethynylsilane and iodobenzene

To a 25 mL nitrogen-flushed, round-bottomed flask which was equipped with a magnetic stirring bar was charged with phenyldimethylethynylsilane (1.0 g, 6.25 mmol), iodobenzene (0.70 mL, 6.30 mmol), anhydrous benzene (10 mL) and anhydrous triethynylamine (6 mL). After stirring for a while, catalytic amount of CuI and $PdCl_2(Ph_3P)_2$ was added. The flask was capped with a rubber septum and the mixture was stirred at room temperature for overnight. Some white salt was slowly precipitated during this period. Following removal of the salt by filtration, most of the benzene and triethylamine were removed on a rotatory evaporator. The organic residue was diluted with 10 mL hexane, and the obtained solution was washed by dilute HCl aqueous solution. After removing the hexane and pumping at ca.0.2 torr, 0.9 g of yellowish liquid was obtained which contained 89% of desired product 57. The product had the following spectral properties. Mass spectrum 236 (23) M^+; 222 (22); 221 (100) M^+-Me. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ -1.18 ($Si-CH_3$); 105.89, 91.09 (acetylenic carbons); 122.13, 126.91, 127.22, 127.92, 128.41, 131.08, 132.76, 136.17 (phenyl carbons). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ -21.537 ppm.

Synthesis of compound (58) via palladium catalyzed coupling between phenyldimethylethynylsilane and 4-iodoanisole

Phenyldimethylethynylsilane (1.2 g, 7.5 mmol) and 4-iodoanisole (2.0 g, 8.5 mmol) were reacted under the same conditions specified for compound 57. After removing salt and solvent, the product was obtained as a mixture of $Ph(Me)_2SiC{\equiv}CH$ (5% by GC), 4-iodoanisole (26%), coupling product 58 (62%), $Ph(Me)_2SiC{\equiv}CC{\equiv}CSi(Me)_2Ph$ (7%). The mixture was directly used to acquire the ^{29}Si NMR spectrum without further purification. ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ -19.138 ppm.

Synthesis of compound (59)

To a 50 mL nitrogen-flushed, round-bottomed flask which was equipped with a magnetic stirring bar, was charged with 15 mL anhydrous THF and $Ph(Me)_2SiC{\equiv}CH$ (1 g, ca. 6.3 mmol). Methylmagnesium chloride (9.0 mmol) was added dropwise into the solution at room temperature through a syringe. After addition the solution was continued to stir for overnight. Acetylchloride (2 mL, 28 mmol) was dissolved in 5 mL anhydrous THF in another 50 mL oven-dried flask. The $Ph(Me)_2SiC{\equiv}CMgCl$ solution prepared above was added into the acetylchloride solution at room temperature. After addition the mixture was continued to stir for two hours. The salt was removed by passing the mixture through a sintered glass filter under an inert atmosphere. The solvent was distilled off under a reduced pressure. The organic residue (ca. 1 mL) contained about 80% of the desired product by GC. The product had the following spectral properties. Mass spectrum 202 (20) M^+; 188 (18); 187 (100) M^+-Me; 160 (12); 159 (87) M^+-43; 145 (63). ^{29}Si NMR ($CDCl_3$, 59.595 MHz) δ -20.645. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ -1.123

(Si-Me); 28.876 (Me); 87.283, 103.926 (C≡C); 127.849, 129.323, 133.724, 136.591 (phenyl carbons); 167.897 (CO).

Synthesis of violet polymer (60)

To a 50 mL nitrogen-flushed, round-bottomed flask which was equipped with a magnetic stirring bar was charged with violet polymer 53 (from WCl_6 catalyst, 140 mg) and anhydrous THF (8 mL). After the polymer was completely dissolved, methylmagnesium chloride (7 mmol) was added at room temperature. The mixture was stirred at room temperature overnight. Then chlorotrimethylsilane (2 ml, 22 mmol) was added dropwise at room temperature through a syringe. Following a stir for half an hour, the excess chlorotrimethylsilane was removed on a rotatory evaporator. To the residue was added 5 mL benzene to help dissolve the polymer. The solution was then added dropwise in methanol (50 mL). The polymer precipitated out was separated by a centrifuge and dried on a vacuum line to a constant weight (125 mg). The obtained polymer had the following spectral properties. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ -0.206 ppm ($Si\text{-}Me_3$, $W_{1/2}$ 0.5 ppm); 13.249 ppm (CH_3, $W_{1/2}$ 1.1 ppm); 19.239 ppm (CH, $W_{1/2}$ 1.2 ppm); 24.987 (CH_2, $W_{1/2}$ 0.8 ppm); vinyl and acetylenic region was shown in figure 23. ^{29}Si NMR ($CDCl_3$, 59.595 MHz) was shown in figure 22. IR spectrum (KBr pellet) ν 2959(s), 2930(s), 2033(w), 1634(m), 1520(w), 1460(m), 1377(w), 1355(w), 1250(m), 1209(w), 1094(w), 1023(w), 999(m), 966(w), 847(s), 764(m), 690(m).

Synthesis of di-n-propyldichlorosilane

In a 1000 mL three-necked flask, n-propylmagnesium bromide (0.84 mol) was prepared from magnesium turnings (20.52 g, 0.84 mol) and 1-bromopropane (76 mL, 0.84 mol) in 440 mL anhydrous ether. In another 2 L nitrogen-flushed, three-necked flask which was equipped with a mechanical stirrer, a condenser and an additional funnel, freshly distilled $SiCl_4$ (46 mL, 0.40 mol) was dissolved in 800 mL anhydrous hexane. The n-propylmagnesium bromide was then added dropwise into the $SiCl_4$ solution while it was vigorously stirred. The addition was slow enough to keep the reaction temperature below 60°C. After addition the mixture was continuously stirred at room temperature overnight. The salt was removed by passing the reaction mixture through a sintered glass filter under an argon atmosphere. GC showed that ca. 70% of the products was dipropyldichlorosilane. Fractional distillation through a 25 cm column gave di-n-propyldichlorosilane (96% pure by GC & GC-MS), bp ~105°C/100 mmHg, in 35% yield.

Synthesis of di-n-butyldichlorosilane

Di-n-butyldichlorosilane was synthesized via the reaction of silicon tetrachloride (34.4 mL, 0.3 mol) with n-butylmagnesium chloride (0.62 mol in 250 mL THF) in 400 mL hexane under the same experimental condition specified for di-n-propyldichlorosilane. Fractional distillation gave 52 grams of colorless liquid at ca. 85°C/45 mmHg with purity 95% by GC (isolation yield 81%).

Synthesis of di-n-hexyldichlorosilane

Di-n-hexyldichlorosilane was prepared via the reaction of silicon tetrachloride (22.9 mL, 0.2 mol) with n-hexylmagnesium bromide (0.42 mol in 220 mL ether) in 500 mL hexane under the same condition specified for di-n-propyldichlorosilane. Fractional distillation gave 40 grams of colorless liquid at 70-110°C/6-0.1 mmHg. GC-MS indicated that ca. 87% of the distillate was di-n-hexyldichlorosilane. The mixture was used in the reaction of preparing di-n-hexyldiethynylsilane without further purification.

Synthesis of di-n-propyldiethynylsilane

In a 250 mL three-necked, argon-flushed, round-bottomed flask equipped with an additional funnel and a magnetic stirring bar, ethynylmagnesium chloride (0.13 mol) was prepared from methylmagnesium chloride (0.13 mol) and acetylene in 120 mL anhydrous THF. The HC≡CMgCl suspension was cooled down to -78°C by a dry-ice bath. Then di-n-propyldichlorosilane (12 g, 0.065 mol) was added dropwise through a syringe. After the addition the temperature was gradually warmed to room temperature and the mixture was stirred for additional three hours. The reaction mixture was cooled to 0°C and 50 mL cold dilute HCl aqueous solution was added. After stirring for a while the organic layer was separated and further washed twice by cold water. Finally the organic layer was dried over anhydrous sodium sulfate. Distillation through a 25 cm helices-packed column gave di-n-propyl-diethynylsilane as a colorless liquid (10 g, yield 46%, purity 99.5% by GC), bp 96-97°C/60 mmHg. The product had the following spectral properties. Mass spectrum 164 (0.5) M^+; 138 (4); 121 (93) $M^+-C_3H_7$; 95 (49); 93 (35); 79 (100); 53 (82). ^1H NMR ($CDCl_3$, 300 MHz) δ 0.74 (t, 4 H), 1.0 (t, 6 H), 1.52 (m, 4 H), 2.45 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 16.535, 16.928, 17.574 (n-propyl);

84.856 (Si-C≡); 95.066 (≡CH, $^{1}J_{CH}$ 239.2 Hz). ^{29}Si NMR ($CDCl_3$, 59.595 MHz) δ -34.595 ppm.

Anal. Calcd for $C_{10}H_{16}Si$: C, 73.09; H, 9.81.

Found: C, 72.73; H, 9.87.

Synthesis of di-n-butyldiethynylsilane

Di-n-butyldiethynylsilane was synthesized via the reaction of di-n-butyldichlorosilane (0.244 mol) with ethynylmagnesium chloride (0.49 mol) under the same conditions specified for the preparation of di-n-propyldiethynylsilane. The obtained reaction mixture was poured portion by portion into cold dilute HCl aqueous solution (250 mL). The organic layer was further washed twice with dilute HCl aqueous solution and then dried with anhydrous sodium sulfate. Fractional distillation of the organic solution afforded di-n-butyldiethynylsilane as a colorless liquid (32.8 g, yield 70%, 99.3% pure by GC), bp 64-65°C/1.5 mmHg. The product had the following spectral properties. Mass spectrum 166 (13) M^+-C_2H; 135 (57) $M^+-C_4H_9$; 110 (36); 109 (64); 107 (92); 79 (100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.75 (t,4 H), 0.90 (t, 6 H), 1.41 (m, 6 H), 2.46 (s, 2 H). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ -33.80 ppm. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 18.50, 18.69, 25.41, 25.79, 84.78, 94.92 ppm. IR spectrum (neat) ν 3292(s), 2958(s), 2927(s), 2873(s), 2041(s), 1466(m), 1406(w), 1379(w), 1344(w), 1298(w), 1273(w), 1082(m), 1028(w), 1001(w), 885(m), 788(m), 758(s), 681(s).

Anal. Calcd for $C_{12}H_{20}Si$: C, 74.92; H, 10.48.
Found: C, 74.90; H, 10.61.

Synthesis of di-n-hexyldiethynylsilane

Di-n-hexyldiethynylsilane was synthesized via the reaction of ethynylmagnesium chloride (0.4 mol) with di-n-hexyldiethynylsilane (a mixture synthesized from 0.42 mole of n-hexylmagnesium bromide and 0.2 mole of silicon tetrachloride) under the same conditions specified for di-n-propyldiethynylsilane. The obtained reaction product was poured portion by portion into 250 mL cold dilute HCl aqueous solution. The organic layer was separated and further washed twice with dilute HCl aqueous solution. Then the organic layer was dried over anhydrous sodium sulfate. Fractional distillation afforded di-n-hexyldiethynylsilane as a colorless liquid (13.6 g, overall yield 27.4%, 100% pure by GC), bp 79-81°C/0.15 mmHg. The product had the following spectral properties. Mass spectrum 223 (2) M^+-C_2H; 222 (9) M^+-26; 194 (7); 163 (26); 138 (11); 135 (24); 121

(31); 109 (30); 107 (42); 105 (17); 95 (25); 93 (16); 83 (11); 81 (20); 79 (100). IR spectrum (neat) ν 3309(m), 2933(s), 2038(m), 1462(w), 1338(m), 1182(w), 966(w). ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ -33.939 ppm. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 2H), 1.20-1.53 (m, 16H), 0.88 (t, J=6.9 Hz, 6H), 0.75 (t, J=8.6 Hz, 4H).

Anal. Calcd for $C_{16}H_{28}Si$: C, 77.34; H, 11.36.

Found: C, 77.24; H, 11.47.

Polymerization of dimethyldiethynylsilane using $Mo(CO)_6$ as catalyst

To a 25 mL oven-dried quartz tube which was equipped with a magnetic stirring bar was charged with carbon tetrachloride (12 mL, distilled over P_2O_5). A flow of argon was bubbled through the solvent for 5 minutes to remove the oxygen. The catalyst $Mo(CO)_6$ (0.060 g, 0.2 mmol) was added and the tube was capped with a rubber septum. The solution was irradiated with UV light at 30°C for an hour and the solution became brown. To this solution was added dimethyldiethynylsilane (2 ml, 1.57 g, 14.5 mmol) via a syringe. After the mixture was heated at 80°C for 20 minutes, a violet jellylike material was formed. After removing solvent and unreacted monomer by pumping at 0.1 mmHg vacuum for two hours, 0.11 gram solid was collected. IR spectrum of the solid showed a weak ethynyl absorption at 2035 and 3279 cm^{-1}. No further characterization was carried out due to the insolubility of the product.

Polymerization of dimethyldiethynylsilane using $MoCl_5$ as catalyst

A solution of dimethyldiethynylsilane (2 ml, 1.57 g) in 25 mL anhydrous THF was placed in an oven-dried, round-bottomed 50 mL flask which was equipped with a magnetic stirrer and capped with a rubber septum. The solution was deoxygenated by freezing, evacuating, refilling with argon and thawing. To the solution was added $MoCl_5$ (0.1 g, 0.2 mmol) in a glove bag under an argon atmosphere. The solution was heated at 80°C for two hours and was dark red. The reaction was stopped by adding the product solution dropwise in 100 mL deoxygenated methanol. The precipitated polymer was separated by filtration and then was redissolved into ca. 50 mL chloroform. After removing the most of the solvent by a rotary evaporator, a beautiful film with golden-green luster was formed. The polymer had the following spectral properties. UV visible spectrum in THF showed λ_{max} 540 nm. The peak molecular weight of the polymer was ca. 50,000. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.425 ppm (Si-CH_3, $W_{1/2}$ 0.3 ppm) 6.0-8.5 ppm broad weak absorption (vinyl protons).

However the soluble product was obtained only once, and the various effort to repeat the experiment failed to produce the soluble polymer product. When using benzene as solvent, the reaction turned to gel in less than 30 minutes at 80°C.

Polymerization of di-n-propyldiethynylsilane using $MoCl_5$ as catalyst

In a 100 mL oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar and capped with a rubber septum, di-n-propyldiethynylsilane (2 ml, 1.60 g) was dissolved in 50 mL anhydrous benzene. After the solution was deoxygenated by freezing, evacuating, refilling with argon and thawing for three times, catalyst $MoCl_5$ (ca.50 mg) was added in a glove bag under an argon atmosphere. After stirring at room temperature for one hour the solution turned blue. The mixture was stirred overnight. Then the blue polymer solution was added dropwise in 150 mL deoxygenated methanol. The precipitated polymer was separated by filtration and dried on a vacuum line (0.1 torr) overnight. A brown polymer powder (0.6 g, yield 37.5%) was obtained. The polymer was soluble in benzene, THF, chloroform and hexane. The polymer had the following spectral properties. UV-visible absorption: λ_{max} 570, 620(sh) nm in THF; 570, 610(sh) nm in hexane; 580, 620(sh) nm in benzene. GPC: Mw = 54,195, polydispersity index 4.01. ^{13}C NMR (CP/MAS) δ 156, 150, 145, 137 ppm broad peaks overlapping each other (vinyl carbons); 16.74 ppm (n-propyl, $W_{1/2}$ 2.5 ppm). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.99 ppm ($W_{1/2}$ 0.2 ppm), 1.42 ppm ($W_{1/2}$ 0.36 ppm), 6.6-7.6 ppm (very weak broad signal). ^{29}Si NMR (CP/MAS) was shown in Figure 26(a).

Polymerization of di-n-butyldiethynylsilane via $MoCl_5$ catalyst

Di-n-butyldiethynylsilane (1.85 g) solution in 50 mL benzene was deoxygenated under the same conditions specified for the polymerization of di-n-propyldiethynylsilane. After the catalyst $MoCl_5$ (ca. 60 mg) was added in a glove bag under an argon atmosphere, the mixture was stirred at room temperature for an hour. Since no violet color was observed, the temperature was raised to 50°C. After 10 minutes a deep violet color was developed in the reaction flask. The mixture was stirred at 50°C overnight (ca. 20 hours). The polymerization was stopped by adding the reaction mixture dropwise into 150 mL deoxygenated methanol. The polymer was separated by filtration and dried on a vacuum line overnight (0.82 g, yield 44%). The polymer had the following spectral properties. UV-visible absorptions: λ_{max} 570, 610(sh) nm in hexane; 580, 620(sh) nm in benzene; 570, 610(sh) nm in THF. GPC: Mw = 87,800, polydispersity index 6.90. ^{13}C NMR (CP/MAS) δ 156, 151, 145, 138 ppm broad peaks overlapping each other (vinyl carbons); 25.15 ($W_{1/2}$ 3 ppm), 12.65 ($W_{1/2}$ 2.2 ppm). ^1H NMR (CD_2Cl_2, 300 MHz) δ 0.9 ppm (s, $W_{1/2}$ 0.15 ppm), 1.4 ppm (s, $W_{1/2}$ 0.2 ppm), 6.0-8.1 ppm (broad weak signals). ^{29}Si NMR was shown in Figure 26(b). IR spectrum (KBr pellet) ν 3292(w), 2957(s), 2924(s), 2871(m), 2035(w), 1636(w), 1527(w), 1464(m), 1385(s), 1296(w), 1263(w), 1190(w), 1080(m), 1026(w), 962(w), 883(m), 810(m), 673(m).

Polymerization of di-n-hexyldiethynylsilane via $MoCl_5$ catalyst

Di-n-hexyldiethynylsilane (1.5 mL, 1.35 g) solution in 50 mL anhydrous benzene was deoxygenated by freezing, evacuating and thawing technique. Catalyst $MoCl_5$ (ca. 60 mg) was added in a glove bag under an argon atmosphere.

A violet color was developed in the flask after the mixture was stirred at 50°C for 15 minutes. After stirred overnight at 50°C, the polymer solution was added dropwise into 150 ml deoxygenated methanol. The polymer was separated by a centrifuge and was dried on a vacuum line overnight. The polymer obtained (0.61 g, yield 45%) had the following spectral properties. UV visible absorptions: 570, 620(sh) nm in THF; 570, 610(sh) nm in hexane. GPC: Mw = 123,440, polydispersity index 5.80. ^{13}C NMR (CP/MAS) 157, 152, 146, 136 ppm broad peaks overlapping each other (vinyl carbons); 30.95 ($W_{1/2}$ 3 ppm), 21.79 ($W_{1/2}$ 2.5 ppm), 13.17 ($W_{1/2}$ 1.5 ppm). ^{29}Si NMR (CP/MAS) spectrum was shown in Figure 26(c).

Polymerization of di-n-hexyldiethynylsilane via WCl_6 catalyst

With the same procedures as in the case of $MoCl_5$ catalyst, di-n-hexyldiethynylsilane (1.80 g) was polymerized in 50 mL of anhydrous toluene in the presence of WCl_6 catalyst (100 mg) at 60°C overnight (violet color occurred after an hour). The polymer was precipitated by addition to 150 mL deoxygenated methanol and separated by filtration. After drying on a vacuum line, 0.98 gram brown polymer was collected (yield 54%). The polymer had the following spectral properties. UV-visible absorption (THF) λ_{max} 543 nm (Figure 28). GPC: Mw = 48,853, PDI = 3.489. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 158, 152, 146, 138 ppm broad peaks overlapping each other (vinyl carbons); 96, 88 ppm (dangling acetylenic carbons); 32.8 ($W_{1/2}$ 0.7 ppm), 31.4 ($W_{1/2}$ 0.4 ppm), 23.8 ($W_{1/2}$ 0.8 ppm), 22.4 ($W_{1/2}$ 0.4 ppm), 13.9 ppm ($W_{1/2}$ 0.4 ppm). ^{29}Si NMR ($CDCl_3$, 59.595 MHz) is shown in Figure 27(a).

Synthesis of diphenyldiethynylgermane (73)

In a 500 mL three-necked, oven-dried, round-bottomed flask equipped with a magnetic stirring bar, an additional funnel, a gas-inlet and an outlet, 0.35 mole ethynylmagnesium chloride was prepared from 0.35 mole methylmagnesium chloride and acetylene in 250 mL anhydrous THF solvent. To the ethynylmagnesium chloride suspension (at -78°C) was added diphenyldichlorogermane (received from Alpha Products, 45 g, 0.15 mole) in THF (40 mL) solution. After the addition the temperature was gradually warmed to room temperature and the mixture was stirred overnight. The product mixture was cautiously poured portion by portion in 150 ml cold dilute aqueous HCl solution. The organic layer was separated in a separation funnel and was further washed twice with cold dilute HCl aqueous solution. The organic layer was finally dried over anhydrous Na_2SO_2. Most of the solvent was removed on a rotatory evaporator and the product was collected at 120-135°C/0.1 mmHg. Recrystallization out of hexane (8 times) gave a white solid (19 g, 36% yield, 99.8% pure by GC), mp 49-50.5°C. The product had the following spectral properties. Mass spectrum 280 (2), 279 (10), 278 (9), 277(45), 276 (19), 275 (34), 274 (8), 273 (24), 227 (3), 226 (2), 225 (2), 204 (7), 203 (10), 202 (11), 201 (25), 200 (9), 199 (20), 197 (15), 178 (8), 177 (11), 176 (31), 175 (43), 174 (31), 173 (28), 172 (18), 171 (20), 155 (3), 154 (19), 153 (7), 152 (6), 151 (15), 150 (6), 149 (15), 148 (4), 147 (12), 145 (4), 102 (11), 101 (12), 100 (2), 99 (56), 98 (15), 97 (42), 95 (33), 78 (5), 77 (56), 76 (16), 75 (10), 74 (31), 73 (7), 72 (16), 70 (13), 63 (5), 62 (1), 52 (8), 51 (100), 50 (38). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.61 (s, 1 H), 7.38-7.48 (m, 3 H), 7.64-7.74 (m, 2 H). IR spectrum (KBr pellet) ν 3251(s), 3071(m), 3061(w), 2031(s), 1485(m), 1435(s), 1385(m), 1362(m), 1310(w), 1186(w), 1096(s), 1026(w), 999(m), 739(s), 712(s), 694(s), 684(s).

Thermal polymerization of diphenyldiethynylgermane

Diphenyldiethynylgermane (1.46 g) was placed in a 5 mL oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar and a condenser. The system was evacuated on a vacuum line and refilled with argon. While a positive argon atmosphere was remained by connecting to a balloon, the monomer was heated at 144-162°C for 20 hours and was gradually solidified at this temperature. The solid would not soften when temperature was raised to 193°C. After an additional two hours at 193°C the reaction was stopped. The product was dark brown solid which was not soluble in benzene. ^{13}C NMR (CP/MAS) δ 127.17 and 133.34 ppm.

Polymerization of diphenyldiethynylgermane (74) using $MoCl_5$ catalyst

Diphenyldiethynylgermane (2.01 g) was dissolved in 25 ml anhydrous benzene in an oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar. The solution was deoxygenated (three times) via freezing, evacuating, refilling with argon and thawing. Catalyst $MoCl_5$ (ca. 50 mg) was added in a glove bag under an argon atmosphere. The solution became violet in a few minutes after the catalyst was added. Then the solution was heated at 50°C overnight. The polymerization was quenched by adding the solution into 200 mL deoxygenated methanol. The polymer was separated by filtration and was dried on a vacuum line overnight (0.8 g, yield 40%). The product was soluble in benzene and chloroform. A beautiful film with metallic luster could be cast from the chloroform solution. The polymer had the following spectral properties. UV-visible spectrum λ_{max} 560 and 600(sh) nm. GPC: Mw = 148,513, PDI = 2.09. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 128.33 ppm ($W_{1/2}$ 1.3 ppm), 134.38 ppm ($W_{1/2}$ 1 ppm).

Polymerization of tetraethynylsilane using $MoCl_5$ catalyst

Tetraethynylsilane (1.2 g, sublimed prior to use) was dissolved in 45 mL anhydrous benzene in a 100 mL oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar. The solution was deoxygenated by freezing, evacuating, refilling with argon and thawing. To this solution the catalyst $MoCl_5$ (ca. 50 mg) was added in a glove bag under an argon atmosphere. The color of the solution was changed to violet after a few minute at room temperature. The mixture was stirred overnight. Lots of fine particles were formed during the reaction. The polymer was precipitated out by adding the reaction mixture in 150 mL deoxygenated methanol and was separated by filtration. The product was brown solid which was exploded when hit by a hammer. IR spectrum of the polymer (KBr pellet) ν 694 (s), 2044 (s), 3277 (s). Due to the explosive properties of the product, no further characterization was carried out.

Synthesis of 1,5-bistrimethylsilyl-3,3-dimethylpenta-1,4-diyne (78)

In a 250 mL oven-dried, nitrogen-flushed flask which was equipped with a magnetic stirring bar and a pressure-equallizing addition funnel, (trimethylsilyl)acetylene (28 mL, 0.2 mol) was dissolved in 120 mL anhydrous THF. To this solution (at 0°C) was added methylmagnesium chloride (0.2 mol, 3 M in THF solution) dropwise through the addition funnel. After the reaction was subsided down the mixture was gradually warmed to room temperature and stirred overnight. Then anhydrous cuprous chloride (0.68 g) was added and the mixture was stirred for 10 minutes. 3-Chloro-3-methyl-1-(trimethylsilyl)-1-butyne 77 (34.9 g, 0.2 mol, synthesized according to the literature procedure[43]) was added at room temperature. over a 15 minutes period. The solution was stirred at 55°C for two hours and then overnight at room temperature. During this period, lots of magnesium salt precipitated. The reaction was quenched with 10% aqueous sulfuric acid (50 mL). The organic layer was separated and was further washed twice with water. Finally the organic layer was dried over anhydrous sodium sulfate and was concentrated on a rotary evaporator. Distillation of the remaining liquid afforded 1,5-bis(trimethylsilyl)-3,3-dimethyl- penta-1,4,-diyne, bp 54-55°C/0.4 mmHg, in 88% yield. The product had the following spectral properties. Mass spectrum 236 (13) M^+; 222 (5); 221 (47) M^+-Me; 179 (51); 149 (17); 148 (100); 123 (15); 73 (74). ^1H NMR ($CDCl_3$, 300 MHz) δ 0.142 ppm (s, 18 H), 1.480 (s, 6 H).

Synthesis of 3,3-dimethylpenta-1,4-diyne (79)

1,5-Bis(trimethylsilyl)-3,3-dimethylpenta-1,4-diyne 78 (41.5 g, 0.176 mol) was dissolved in 120 mL dry n-butanol in a 250 mL round-bottomed flask which was equipped with a magnetic stirring bar. The solution was cooled to 0°C and a catalytic amount of potassium hydroxide (2 g) was added. The flask was capped with a rubber septum and the solution was stirred overnight at room temperature. Then 100 mL water and 70 ml pentane was added into the reaction mixture. The organic layer was separated and washed by 5% HCl aqueous solution and then by water. The organic layer was dried over anhydrous sodium sulfate. Fractional distillation through a 25 cm column which was packed with glass helices afforded a colorless liquid (12.7 g) at 72-74°C. Based on the integration in ^1H NMR and GC-MS, the liquid contained ca. 2% $Me_3SiOSiMe_3$ and 98% 3,3-dimethylpenta-1,4-diyne. The product was used in the following polymerization studies without further purification. The product had the following spectral properties. Mass spectrum 92 (9) M^+; 91 (100) M^+-H; 77 (60) M^+-Me; 51 (69); 50 (22). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.538 ppm (s, 6 H), 2.225 (s, 2 H).

Polymerization of 3,3-dimethylpenta-1,4-diyne using $MoCl_5$ as catalyst

3,3-Dimethylpenta-1,4-diyne (1.1 g) and anhydrous benzene (40 mL) was mixed in a 100 mL oven-dried, round-bottomed flask which was equipped with a magnetic stirring bar. The solution was deoxygenated by freezing, evacuating, refilling with argon and thawing. The catalyst $MoCl_5$ (ca. 50 mg) was added in a glove bag under an argon atmosphere. The solution was heated to 50-60°C for overnight. The polymer was precipitated by dropwise addition to 150 mL deoxygenated methanol and was separated by filtration. The obtained yellow brown solid was dried on a vacuum line (0.1 torr) for overnight (0.44 g, yield 40%). The polymer had the following spectral properties. UV-visible spectrum (THF) exhibited a long tail extended from 220 nm to 640 nm (no λ_{max} between 220-700 nm). GPC: Mw = 24,550, PDI = 4.50. IR (KBr pellet) ν 3308(m), 2972(s), 2932(m), 2108 (vw), 1597(w), 1464(m), 1385(m), 1362(m), 1219(w), 878(w), 716(vw). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.5 ppm (broad signal, $W_{1/2}$ 0.43 ppm). ^{13}C NMR (CP/MAS) δ 29.68 (br, CH_3, $W_{1/2}$ 17 ppm); 69.66 (br, $W_{1/2}$ 13 ppm), 90.36 (br, $W_{1/2}$ 6 ppm), about 25-30% not reacted acetylenic carbons; 122.4 (br, $W_{1/2}$22.5 ppm), 136.0 (br, $W_{1/2}$ 15 ppm).

<u>Oxidative coupling of 3,3-dimethylpenta-1,4-diyne using CuCl/O_2</u>

In a 100 mL three-necked, round-bottomed flask which was equipped with a magnetic stirring bar, a gas inlet and an outlet, was added benzene (50 mL), pyridine (1.7 mL), N,N,N',N'-tetramethylethylenediamine (0.15 g, 1.5 mmol) and copper(I) chloride (0.15 g, 1.5 mmol). After the solution was warmed to 60-70°C, 3,3-dimethylpenta-1,4-diyne (1.8 g) was added dropwise to the solution while an oxygen bubbling was maintained. After addition the mixture was continued to stir at 60°C for 20 minutes with oxygen bubbling. The reaction mixture was washed by 50 mL 10% sulfuric acid aqueous solution, and then by water. The organic layer was dried over anhydrous Na_2SO_4. After removing the solvent, a white solid (mp 155-165°C, 1.46 g, yield 81%) was collected. The polymer had the following spectral properties. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.229 (1 H), 1.520 (230 H). ^{13}C NMR ($CDCl_3$, 300 MHz) δ 80.83, 64.94, 30.27 (CH_3), 26.90. GPC: Mw = 1029, PDI = 1.85.

Synthesis of bis(dimethylsilyl)methane[49]

In a 2L round-bottomed flask which was equipped with a magnetic stirring bar and a condenser was added anhydrous THF (1000 mL), dimethylchlorosilane (327 mL, 3.0 mol), methylenechloride (64 mL, 1.0 mol), magnesium turnings (48.6 g, 2.0 mol) and zinc powder (6.0 g). The mixture was stirred at 50°C for 24 hours. Lots of white salt was precipitated out from the reaction during this period. The salt was removed by filtration. The excess dimethylchlorosilane and THF solvent was separated from the product by fractional distillation. Finally 49 grams bis(dimethylsilyl)methane was collected, b.p.103-104°C, yield 37%. Mass spectrum 132 (3) M^+; 118 (16); 117 (100) M^+-Me; 73 (90); 59 (39); 45 (29).

Synthesis of bis(chlorodimethylsilyl)methane

In a 250 mL round-bottomed, nitrogen-flushed flask which was equipped with a magnetic stirring bar and a condenser was added bis(dimethylsilyl)methane (17.58 g, 0.133 mol), CCl_4 (125 ml, freshly distilled from P_2O_5) and catalytic amount of benzoyl peroxide (0.3 g). The solution was refluxed for overnight. Fractional distillation afforded bis(chlorodimethylsilyl)methane as a colorless liquid (23.8 g, yield 90%), bp ca.95°C/50 mmHg. Mass spectrum 191 (1.0); 190 (2.3); 189 (16.5); 188 (11.4); 187 (74.8); 186 (17.2); 185 (100) M^+-15; 171 (2.1); 169 (3.0); 168 (1.1); 167 (6.0); 166 (2.7); 165 (14.9); 151 (5.4); 150 (2.3); 149 (16.5); 141 (1); 135 (2.1); 133 (1.9); 121 (1.1); 119 (1.7); 93 (15.2); 73 (36.9).

Synthesis of bis(ethynyldimethylsilyl)methane (82)

In a 500 mL round-bottomed, three-necked flask which was equipped with a magnetic stirring bar, a gas inlet and an outlet, 0.24 mol ethynylmagnesiumchloride was prepared from methylmagnesium chloride (0.24 mol) and acetylene in 300 mL THF. The HC≡CMgCl suspension was cooled to -78°C and then bis(chlorodimethylsilyl)methane (23.8 g, 0.119 mol) was added. After addition the mixture was gradually warmed to room temperature and stirred for three hours. Then the reaction mixture was poured portion by portion in 150 mL cold dilute HCl aqueous solution. The organic layer was separated and further washed twice with cold dilute HCl aqueous solution. Finally the organic layer was dried over anhydrous Na_2SO_4. Fractional distillation afforded bis(ethynyldimethylsilyl)methane 82 (20.4 g, yield 95.3%, 99.3% pure), bp 88-90°C/50 mmHg. The product had the following spectral properties. Mass spectrum 167 (9); 166 (20); 165 (100) M^+-Me; 139 (5); 107 (8); 93 (17); 83 (26); 73 (12); 69 (12); 67 (17); 55 (15); 53 (19). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.053 (s, 2 H); 0.264 (s, 12 H); 2.399 (s, 2 H).

Polymerization of bis(ethynyldimethylsilyl)methane (82) using $MoCl_5$ catalyst

Bis(ethynyldimethylsilyl)methane (1.4 g) was dissolved in 40 mL anhydrous benzene in a 100 mL oven-dried flask which was equipped with a magnetic stirring bar. The solution was deoxygenated by freezing, evacuating, refilling with argon and thawing technique. Catalyst $MoCl_5$ (ca.60 mg) was added in a glove bag under an argon atmosphere. Then the flask was capped with a rubber septum and the solution was heated at 60°C under a positive argon pressure for 24 hours. The obtained brown polymer solution was added dropwise into 150 mL deoxygenated methanol. The precipitated brown powder (0.6 g, 43% yield) was separated by filtration and dried on a vacuum line overnight. The polymer had the following spectral properties. GPC: Mw 12,477, PDI 4.0. UV-visible spectrum (hexane) λ_{max} 260 nm, 420 nm. IR (KBr pellet) ν 2955(s), 2899(w), 1433(w), 1406(vw), 1350(vw), 1250(s), 1096(m), 1049(s), 996(s), 831(vs), 765(vs), 735(m), 694(m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ -0.4-0.7 ppm. ^{29}Si NMR ($CDCl_3$, 59.595 MHz) δ 9.85 ($W_{1/2}$ 0.9 ppm, 30%), 8.70 ($W_{1/2}$ 0.37 ppm, 40%), -3.93 ($W_{1/2}$ 0.25 ppm, 30%).

Polymerization of bis(ethynyldimethylsilyl)methane (82) using WCl_6 catalyst

Bis(ethynyldimethylsilyl)methane 82 (1.69 g) was polymerized in 25 mL anhydrous toluene in the presence of WCl_6 catalyst (ca. 120 mg) according to the same procedure as in the case of $MoCl_5$ catalyst. After precipitated out of 150 mL deoxygenated methanol and dried on a vacuum line, a brick red powder was obtained in 88% yield. The polymer had the following spectral properties. UV-visible spectrum λ_{max} 260 nm, 440 nm. GPC: Mw 11,330, PDI 3.9. ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 1.33 ppm (CH_3 and CH_2, $W_{1/2}$ 2 ppm), vinyl and acetylenic region is shown in Figure 34. ^{29}Si NMR ($CDCl_3$, 59.591 MHz) δ 9.7 ppm, 8.6 ppm, 1.5 ppm, -4.1 ppm, -17.6 ppm.

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SUMMARY

Several new types of silicon-containing preceramic polymers, i.e., poly(diorganosilacetylene) and poly(diorganosilvinylene) have been synthesized with molecular weights from 10,000 to 120,000. These polymers could be thermally converted to SiC with a moderate to high char yields. Ready solubility and good processability made these types of polymers even more attractive in their applications to ceramics.

First example of copolymer which contains alternate $-SiMe_2-C{\equiv}C-$ and $-SiMe_2-CH{=}CH-$ units was successfully synthesized. This copolymer had a dramatically lower decomposition temperature (300°C) and high char yield.

The thermal polymerization of diethynyldiphenylsilane, which was reported in 1968 to afford poly(diphenylsildiacetylene) $(Ph_2Si-C{\equiv}C-C{\equiv}C)_n$ via dehydrogenation, was reinvestigated. Spectroscopic studies showed that the polymer had a structure of polyacetylene type not diacetylene.

Diphenyldiethynylgermane and a series of diorganodiethynylsilanes were synthesized. These diethynyl- silane or germane could be polymerized in the presence of $MoCl_5$ or WCl_6 to afford a soluble, violet

material with Mw as high as 108,000 (PDI ca. 2). The violet polymer was found to have a four-membered ring structure from cyclopolymerization of diorganodiethynylsilane monomer. The polymer was intrinsically an electrical insulator. Brief exposure of the polymer film to I_2 vapor could increase the conductivity up to 0.1 s/cm. The non-linear $\chi^{(3)}$ value at 625 nm was measured to be $3x10^{-9}$ esu, one of the largest measured among π-conjugated polymers. Photobleaching recovery at 2 ev, measured with 75 fsec resolution, was 300 femtosecond ($3x10^{-13}$ second) which is the fastest ever observed in the π-conjugated polymers.

As a structural model study for cyclopolymerization of 1,6-heptadiyne, bis(ethynyldimethylsilyl)methane was polymerized by using $MoCl_5$ or WCl_6 catalyst to afford a red polymer with UV λ_{max} 440 nm. The structure of the polymer was first confirmed spectroscopically as a six-membered ring.

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