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# Thermal and Catalytic Polymerization of Diethynyldiphenylsilane

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ABSTRACT: The thermal polymerization of diethynyldiphenylsilane, reported in 1968 to afford the poly(silylenebutadiyne), $-[Ph_2Si-C\equiv C-C\equiv C]_n-$, has been reinvestigated and found not to produce a polymer containing acetylenic units in the chain. Vastly improved properties are achieved when the polymerization is catalytically induced with $MoCl_5$ or $WCl_6$. These polymers are electrically conducting ($10^{-3}$ S/cm) with $I_2$ doping and form good-quality solvent-cast films.

## Introduction

In 1968 Luneva, Sladkov, and Korshak[1] reported that heating a neat sample of diethynyldiphenylsilane (1) in a nitrogen atmosphere at 150 °C for 20 h, followed by 8 h at 200 °C, produced a brick red, brittle polymer of molecular weight 3500 that softened at 160–180 °C and was soluble in several organic solvents. The structure of this polymer was assumed to be that of repeating diphenylsilylene-1,3-butadiyne units (3) since $H_2$ evolved from the polymerization. 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.

$$\underset{1}{Ph_2Si(C{\equiv}CH)_2} \xrightarrow[-H^{\bullet}]{\Delta} \underset{2}{HC{\equiv}C\text{-}Si(Ph_2)\text{-}C{\equiv}C^{\bullet}} \xrightarrow{2} HC{\equiv}C\text{-}Si(Ph_2)\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}Si(Ph_2)\text{-}C{\equiv}CH \rightarrow\rightarrow\rightarrow \underset{3}{-[Si(Ph_2)\text{-}C{\equiv}C\text{-}C{\equiv}C]_n-}$$

The proposed mechanism for the thermal polymerization of 1 is clearly incorrect since the acetylenic C–H bond is far too robust for homolysis to facilely occur at the reported temperatures. Thus, given our general interest in polymers containing alternating silicon and unsaturated carbon,[2] we undertook a reinvestigation of the thermal polymerization of 1.

## Results and Discussion

**Structural Investigation of the Thermal Polymer of $Ph_2Si(C{\equiv}CH)_2$.** Heating neat diethynyldiphenylsilane (1) at 150 °C for 18 h 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.* While the yield of red polymer was ca. 90%, the production of acetylene was <2%.

It was assumed that the thermal polymerization of 1 was a free-radical process. Evidence in support of this assumption was obtained by heating 1 dissolved in $Cl_3CCCl_3$ at 210 °C for 18 h with 98% recovery of unreacted 1. Since the alkyl chlorides are excellent silyl radical traps,[3] this strongly indicates that the thermal polymerization of 1 proceeds by initial homolysis of a Si–C bond to produce the initiating silyl radicals. That the absence of polymerization in hexachloroethane was not simply due to the fact that 1 was in solution was demonstrated by successfully conducting the thermal polymerization of 1 dissolved in xylene or in diphenyl ether.

If indeed the polymer from 1 contained the silylbutadiyne units of structure 3, 1,3-butadiyne should be liberated by base-induced decomposition since silylacetylenes are extremely susceptible to cleavage by nucleophilic attack on silicon.[4] Thus the red polymer was decomposed by heating with $D_2O$ containing 12% NaOD, and the resulting volatiles were analyzed by GCMS. Approximately 1% $DC{\equiv}CD$ was found but no $DC{\equiv}C\text{-}C{\equiv}CD$.

Structural analysis of the red polymer by $^1H$ NMR and $^{13}C$ NMR is hampered by the dominance of the aromatic hydrogens and carbons (Figures 1 and 2). Since only weak absorptions for acetylenic carbons ($\delta$ 85 and 98) are observed and these can be attributed to unreacted, "dangling" $C{\equiv}CH$ units, which are also observed in the IR spectrum ($\nu(C{\equiv}CH) = 3267\ cm^{-1}$), it may be presumed that the polymer is a polyolefin. $^{29}Si$ NMR spectra obtained both in solution and in the solid state (Figures 3 and 4) revealed silicons in a wide variety of magnetic environments, and thus the red polymer of 1 is not regular and must be highly branched.

The most conclusive evidence for the elimination of 3 as the structure of the thermal polymer of 1 came from an unambiguous synthesis of 3.[5] Extrapolating from the observation of Ballard and Gilman[6] that hexachlorobutadiene (4) is completely dechlorinated by reaction with magnesium, we found that treatment of 4 with 4 equiv of *n*-BuLi in THF at −78 °C followed by quenching with $Ph_2SiCl_2$ affords 3 as a light yellow solid ($M_w$ = 10 000) characterized as 3 by $^1H$ NMR (only aromatic H's), $^{13}C$ NMR (Figure 5, acetylenic C's at $\delta$ 80.36 and 91.45), and $^{29}Si$ NMR (single sharp peak at $\delta$ −47). Base-induced decomposition of 3 using NaOD in $D_2O$ does indeed produce dideuterio-1,3-butadiyne in ca. 90% yield as determined by GCMS. Thus it is conclusively established that thermal polymerization of $Ph_2Si(C{\equiv}CH)_2$ does not produce polymer 3.

$$\underset{4}{Cl_2C{=}C(Cl)\text{-}C(Cl){=}CCl_2} \xrightarrow{n\text{-}BuLi} [Li\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}Li] \xrightarrow{Ph_2SiCl_2} \underset{3}{-[Si(Ph_2)\text{-}C{\equiv}C\text{-}C{\equiv}C]_n-} \xrightarrow[NaOD]{D_2O} DC{\equiv}C\text{-}C{\equiv}CD$$

**Catalytic Polymerization of 1.** Recently, Cho[7] has reported that dipropargyl derivatives 5 are cyclopolymerized with the metathesis catalysts $MoCl_5$ and $WCl_6$.

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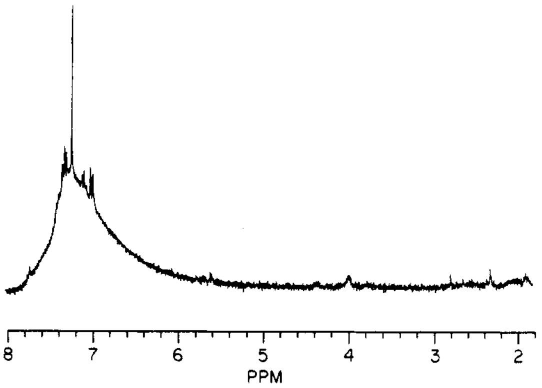


**Figure 1.** $^1$H NMR spectrum of the thermally polymerized 1 in $DCCl_3$.

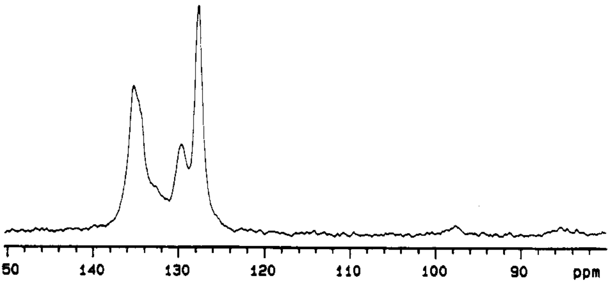


**Figure 2.** $^{13}$C NMR spectrum of the thermally polymerized 1 in $DCCl_3$.

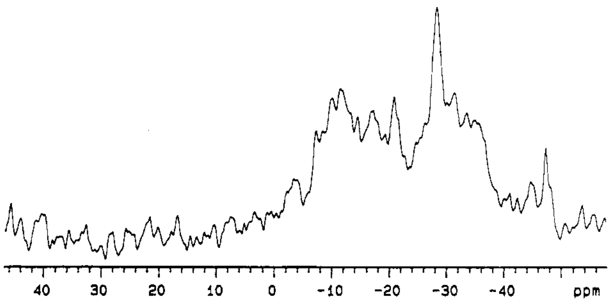


**Figure 3.** $^{29}$Si NMR spectrum of the thermally polymerized 1 in $DCCl_3$.

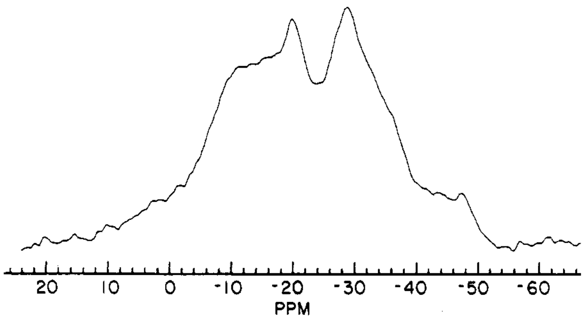
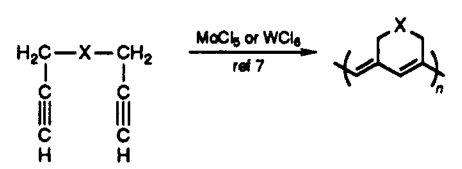


**Figure 4.** Solid-state $^{29}$Si NMR spectrum of the thermally polymerized 1.



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X = O, S, GeR$_2$, SiR$_2$

In striking contrast to thermal polymerization we find that polymerization of $Ph_2Si(C\equiv CH)_2$ catalyzed by either $MoCl_5$ or $WCl_6$ affords a deep violet polymer (6) of vastly improved molecular weight (Table I).

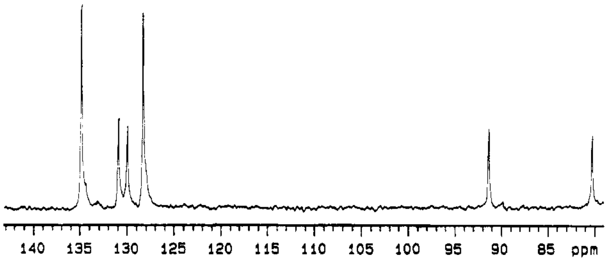
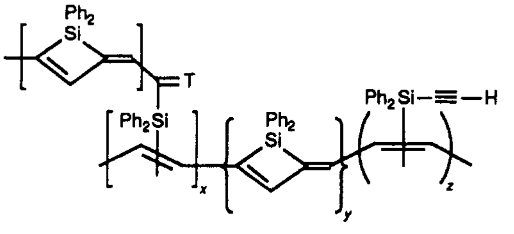


**Figure 5.** $^{13}$C NMR spectrum of polymer 3 in $DCCl_3$.

$$Ph_2Si(C\equiv CH)_2 \xrightarrow{\text{cat.}} \underset{\mathbf{6}}{\text{violet polymer}}$$

The UV-visible spectrum of 6 is strikingly different (Figure 6) from that of thermally polymerized 1, with the $\lambda_{max}$ of ca. 540 nm indicating extensive conjugation. While solvent-cast films of 6 are electrically insulating, exposure to iodine vapor immediately increases the conductivity to $10^{-3}$ S/cm. $I_2$ doping turns the film black, but, upon pumping, the film gradually reverts to its original violet color and insulating character.

As to the structure of 6, the $^1$H NMR and $^{13}$C NMR spectra are dominated by absorption from the phenyl groups and are thus relatively uninformative. The solid-state $^{29}$Si NMR spectrum of polymer 6 (Figure 7) shows absorption from ca. −10 to −50 ppm and is considerably broadened even though magic-angle spinning was employed. However, the $^{29}$Si NMR spectrum (Figure 8) reveals a far more ordered structure than for the thermally produced polymer (see Figures 3 and 4) with one dominant sharp peak at $\delta$ −21.5 suggesting a regular repeating unit. We suggest that this unit is a methylenesilacyclobutene (7) and the polymer chain randomly contains acyclic olefinic units with the associated silicons possessing either dangling acetylenes or branching olefins. The resonance at ca. −30 ppm is assigned to silicon bearing a dangling acetylene based on the shifting of this peak when the acetylenes were silylated with base/$Me_3SiCl$. It is assumed that the silicons attached to two acyclic olefinic units (−10 to −20 ppm) are chain branches, arising from initiation of polymerization on a dangling acetylene, since significant cross-linking would render the polymer insoluble. The detailed structural determination of catalytically polymerized diethynylsilanes will be discussed in detail in a forthcoming article dealing with dialkyl-substituted systems and their nonlinear optical properties.



T = undefined chain terminator

## Experimental Section

**Instruments for Characterization.** Infrared spectra were obtained from KBr pellets and recorded on an IBM Model IR/98 FT-IR. $^1$H NMR spectra were obtained from $CDCl_3$ solutions and recorded on a Nicolet Model NT 300-MHz FT spectrometer. Solid-state $^{29}$Si NMR spectra were obtained on a Bruker MSL 300 spectrometer. Solution $^{29}$Si NMR and $^{13}$C NMR spectra were obtained in $DCCl_3$ with a Varian VXR 300 and were acquired under quantitative condition by using an inverse gated decoupling pulse sequence. Ultraviolet absorption spectra were

Table I
Catalytic Polymerization of Diethynyldiphenylsilane

| monomer | cat. | temp/°C | solvent | % yield | color | $M_w$ |
|---|---|---|---|---|---|---|
| 1 | $Mo(CO)_6$-$h\nu$ | 80 | $CCl_4$ | 10 | red | 10 000 |
| 1 | $MoCl_5$ | 60 | benzene | 54 | violet | 105 308 |
| $Ph_2Si(C{\equiv}CD)_2$ | $MoCl_5$ | 60 | benzene | 53 | violet | 100 000 |
| 1 | $WCl_6$ | 25 | toluene | 51 | violet | 34 000 |

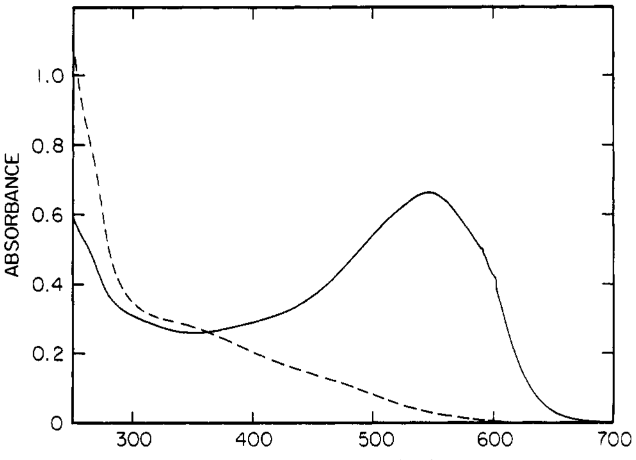


**Figure 6.** UV-visible spectra (THF) of poly(diethynyldiphenylsilane) from thermal (dashed line) and catalytic (solid line) polymerization.

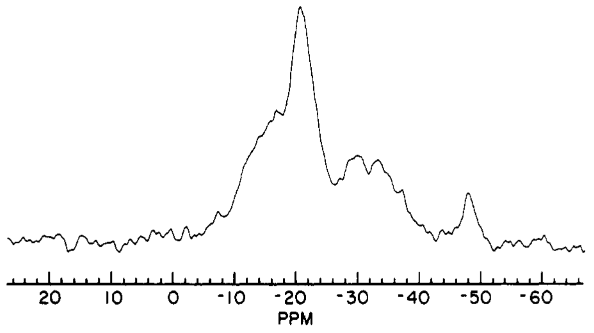


**Figure 7.** Solid-state $^{29}$Si NMR spectrum of the thermally polymerized 1.

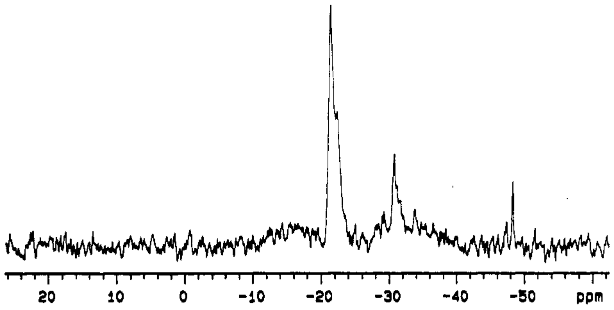


**Figure 8.** $^{29}$Si NMR spectrum ($DCCl_3$) of polymer 6 made with $WCl_6$ catalyst.

measured in THF with a Perkin-Elmer Model 320 UV-vis spectrometer. Molecular weights were obtained by gel permeation chromatography (GPC) with retention times calibrated against nine narrow-dispersity polystyrene samples (Polymer Labs). GPC analyses were performed on a Perkin-Elmer Series 601 liquid chromatograph equipped with a Waters Associates R401 RI detector and a Nelson analytical data system. Five $\mu$-Styragel columns ($10^6$, $10^5$, $10^4$, $10^3$, 500 Å) were employed in series with a flow rate of 1 mL/min.

Tungsten(VI) and molybdenum(V) chloride (Aldrich), tetraphenyltin (Alpha Products), and methylmagnesium chloride (Aldrich) were used as purchased. Dichlorodiphenylsilane and solvents were purified by distillation over $CaH_2$. Diethynyldiphenylsilane is reported but not fully characterized in the literature.[8]

**Preparation of Diethynyldiphenylsilane (1).** Dichlorodiphenylsilane (25.32 g, 0.1 mol) diluted with THF (20 mL) was added during 0.5 h to a solution of ethynylmagnesium chloride prepared from acetylene and methylmagnesium chloride (70 mL of a 3 M solution in THF) at ice temperature. The mixture was initially stirred at 20 °C for 2 h, then refluxed for 30 min, and allowed to stand at room temperature for 12 h. Dilute HCl was added slowly and organic products were extracted with hexanes. The extracts were dried, and solvent removal under reduced pressure gave a pale yellow oily product that was fractionated to give diethynyldiphenylsilane: yield 86%; bp 134–136 °C/0.2 Torr (lit.[8] bp 162 °C/4 Torr); mp 45 °C (lit.[8] mp 45 °C); $^1$H NMR ($CDCl_3$) $\delta$ 7.78–7.73 (2 H, m, ArH), 7.43–4.35 (3 H, m, ArH), 2.74 (1 H, s, $C{\equiv}CH$); $^{13}$C NMR ($CDCl_3$) $\delta$ 134.65, 131.21, 130.52, 128.15 (Ar), 97.41, 83.31 (Si–$C{\equiv}C$); $^{29}$Si NMR ($CDCl_3$) $\delta$ −48.02.

**Thermal Polymerization of 1.** Diethynyldiphenylsilane (1.7 g) was placed in an argon-flushed, 5-mL, one-necked, round-bottomed flask that was equipped with a magnetic stirrer. Heating this monomer at 155 °C for 20 h produced a miniscule amount of acetylene, which was separated and analyzed by GCMS and replaced with dry argon. The color of the liquid mixture changed to red during this initial heating, and upon further heating at 200 °C for 8 h, the mixture was brick red and very viscous. The polymerization was stopped by cooling to room temperature. A clear, hard, dark red solid polymer was obtained, which was soluble in THF, benzene, and $CHCl_3$. The polymer was precipitated from THF solution with methanol, separated by centrifugation, and dried under vacuum over 24 h. Polymer yield was ca. 90%, with weight-average molecular weight of $M_w$ = 19 000 from GPC using polystyrene standards. Higher molecular weight polymers were obtained by longer heating at 200 °C, but these had much lower solubilities.

**Catalytic Polymerization.** All procedures for catalyst preparation and polymerization were carried out under a dry argon atmosphere. A typical catalytic polymerization procedure is as follows: A solution of 2.0 mL of 1 in 25 mL of anhydrous benzene was placed in an argon-flushed, 50-mL, one-necked, round-bottomed flask that was equipped with a magnetic stirrer and capped with a rubber septum. The solution was degassed by repeating a cycle of freezing and thawing under vacuum for four cycles, followed by covering with an argon atmosphere. $MoCl_5$ (50 mg) was added to the solution to immediately produce a deep violet colored material. After the solution was magnetically stirred at 60 °C for 15 h, the polymerization was terminated by dropwise addition of the reaction mixture to 150 mL of methanol. The precipitated polymer was separated by centrifugation and dried to a constant weight under vacuum over 24 h. The polymer yield was ca. 50%. The polymer was soluble in a variety of organic solvents, e.g., benzene, chloroform, and toluene. Polymer films that were cast from chloroform solution had a golden metallic sheen. The films were found to be quite stable to the atmosphere and maintained their color, pliability, and doped-conduction ability after several days of atmospheric exposure.

**Conductivity.** The electrical conductivity (two probe under vacuum) of the films was measured by solution casting the films onto a glass substrate coated with Al pads. The pristine undoped films were insulators with $\sigma = 10^{-9}$ S/cm, which immediately increased to $10^{-3}$ S/cm upon doping with iodine vapor. The doping levels were measured by the weight uptake method. Although up to 5 wt % doping was studied, the maximum conductivity was essentially achieved in the first 2 min of exposure to $I_2$ vapor.

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## References and Notes

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**Registry No.** 1, 1675-57-6; 1 (homopolymer), 52016-42-9; $Ph_2SiCl_2$, 80-10-4; $Mo(CO)_6$, 13939-06-5; $MoCl_5$, 10241-05-1; $Ph_2Si(C{\equiv}CD)_2$ (homopolymer), 131236-74-3; $WCl_6$, 13283-01-7; $D_2O$, 7789-20-0; NaOD, 14014-06-3; $I_2$, 7553-56-2; ethynylmagnesium chloride, 65032-27-1.