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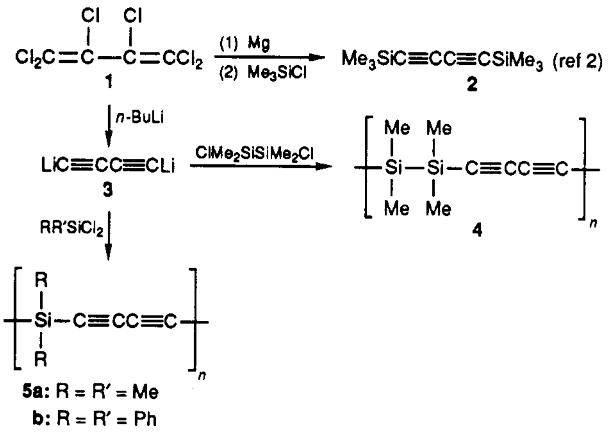
Synthesis and Study of Silylene–Diacetylene Polymers

Recently we reported[1] that trichloroethylene, $Cl_2C{=}CHCl$, is cleanly converted by *n*-butyllithium to dilithioacetylene, $LiC{\equiv}CLi$, from which in situ quenching with R_2SiCl_2 produced the silylene–acetylene polymers, $\{R_2SiC{\equiv}C\}_n$. Thermal conversion of these polymers to silicon carbide/carbon revealed that neither the acetylenic carbons nor the silicon volatilized and thus always remained in the char. We now report that silylene–diacetylene polymers of relatively high molecular weights can be conveniently prepared by a similar "one-pot" route.

In 1968 Gilman[2] reported that magnesium-induced dechlorination of hexachlorobutadiene (**1**) followed by quenching with Me_3SiCl afforded bis(trimethylsilyl)butadiyne (**2**). In our hands attempted extrapolation of this chemistry to the production of silylene–diacetylene polymers through quenching with dichlorosilanes did not produce materials with acceptable molecular weights. However, it was found that **1** is cleanly converted to dilithiobutadiyne (**3**) through reaction with 4 equiv of *n*-BuLi in THF, and quenching of the resulting solution with various dichlorosilanes or dichlorotetramethyldisilane affords the desired polymers **4** or **5**, respectively, in excellent yields.[3]

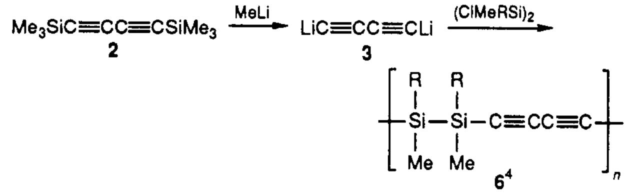


5a: R = R′ = Me
b: R = R′ = Ph
c: R = Ph, R′ = Me

Characterization of polymers **4** and **5** was by GPC, IR, ^1H NMR, ^{13}C NMR, and ^{29}Si NMR. Pertinent data from these analyses are included in Table I. All the polymers are light yellow to brown powders that are soluble in a variety of organic solvents, such as benzene, THF, and chloroform.

Ishikawa[4] has recently reported the synthesis of two disilylene–diacetylene polymers, **6a** and **6b**, by generating **3** through the reaction of **2** and methyllithium followed by quenching with $(MeEtSiCl)_2$ or $(MePhSiCl)_2$.[5]

In contrast to Ishikawa's observation[4] that polymers **6** become strongly conducting (**6a**, 1.04 S/cm; **6b**, 0.38 S/cm), when treated with SbF_5 vapor, exposure of spun films of **5c** to I_2 or AsF_5 vapors produced conductivities only of ca. 10^{-7} S/cm, a magnitude that can be achieved with virtually any polymer (e.g., polystyrene). However, when doping of **5c** was conducted by stirring a methylene chloride solution of **5c** and $FeCl_3$ for 12 h, a cast film from this mixture had a conductivity of ca. 10^{-4} S/cm.



	yield, %	M_w	M_w/M_n
6a (R = Ph)	19	44400	9.27
6b (R = Et)	56	4800	2.75

With regard to the thermal properties of diacetylene polymers **4** and **5**, TGA analysis reveals a remarkable similarity for each of these four polymers in that by 1000 °C they have experienced only a 20% weight loss (see Table II). These high char yields are almost certainly due at least in part to thermally induced cross-linking. Polymers of the $\{XC{\equiv}CC{\equiv}C\}_n$ type, with X being an aromatic or heteroaromatic ring, have been independently reported by Economy,[8] Whitesides,[9] and Stille[10] to undergo "hypercrosslinking" above 150 °C. Indeed, DSC analysis in argon of polymers **4**, **5a**, and **5c** reveals in each case a strong exotherm (Table II) with onset between 100 and 150 °C. The one exception is polymer **5b**, which reproducibly displays three exothermic maxima at 170, 265, and 322 °C. The exotherms decrease in magnitude but continue to ca. 600 °C, and this secondary plateau can be attributed to the decomposition reactions that accompany the losses of benzene and methane. Determination of the evolved gases was achieved by conducting the polymer pyrolyses in an evacuated quartz tube connected to a quadrupole mass spectrometer. As only benzene (**5b**, **5c**), methane (**4**, **5a**, **5c**), and hydrogen are observed, it again[1] appears that only the substituents on silicon are lost in the thermolysis of $SiC{\equiv}C$ polymers. Although crystalline 1,3-diynes are well-known[11] to polymerize to a conjugated chain with alternating double and triple bonds, ^{13}C NMR analysis of thermally cross-linked **4** and **5** shows no evidence for sp-hybridized carbons. Similar observations have been made for other thermally cross-linked diyne polymers.[8-10] X-ray powder diffraction analysis of the chars after heating to 1000 °C shows the formation of β-silicon carbide, SiC. Both ESCA and elemental analysis indicate carbon and silicon as the exclusive elemental components of the char. Combustion analyses of the chars (for carbon, subtracting for silicon) show considerable substituent control on the production of SiC (Table II). In general, phenyl substitution produces lower percentages of SiC in the char, an effect that we have previously observed for silylene–acetylene polymers.[1]

Although we do not observe distinct melting endotherms in the DSC traces, the polymers possessing phenyl substituents on silicon, **5b** and **5c**, visually appear to melt at ca. 120 °C. From these melts good quality fibers can be pulled, the fibers can be cross-linked either thermally or with ultraviolet light, and firing to 1200 °C occurs without loss of the fiber shape. Likewise, pressed pellets of these polymers undergo densification when fired in vacuo, and

Table I

polymer	yield, %	M_w	M_w/M_n	$\nu_{C\equiv C}$, cm^{-1}	NMR (δ) (SiMe) $^1H/^{29}Si/^{13}C$	NMR (δ) ($C{\equiv}CC{\equiv}C$–) ^{13}C
5a	94	20 000	1.7	2073	0.37/−37/−0.6	82, 89
5b	91	10 000	2.2	2077	—/−47/—	80.5, 91.8
5c	92	20 000	1.6	2070	0.55/−44/0.6	81, 91
4	96	20 000	2.0	2062	0.26/−38.2/−3.0	84.6, 91.2

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Table II

polymer	TGA[a] (wt % char at 1000 °C)	DSC[b] exotherm max, °C	DSC[b] integrated to 600 °C, cal/g	combustn anal. of char, wt % C	combustn anal. of char, wt % calcd for SiC
4	82	268	534	58.71	59
5a	82	203	39	72.04	40
5b	80	265	322[c]	83.6	23.4
5c	79	212	366	76.4	33.7

[a] Helium flow; 20 °C/min. [b] Argon flow; 10 °C/min. [c] Smaller maxima at 170 and 322 °C.

the resulting ceramic pellets are extremely strong. We are currently measuring the properties of these materials, and these will be reported in due course.

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References and Notes

(1) Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955.
(2) Ballard, D. H.; Gilman, H. *J. Organomet. Chem.* **1968**, *15*, 321.
(3) In a typical experiment, 10 mL (0.064 mol) of **1** was added dropwise to a stirred, −78 °C solution of *n*-BuLi (0.255 mol, 105 mL of 2.5 M in Skelly B) and THF (50 mL). After addition, the mixture was allowed to warm to room temperature and stirred for 2 h. A small aliquot was quenched with Me_3SiCl and then hydrolyzed with dilute aqueous HCl. GCMS analysis of the organic layer showed **1** completely consumed and **2** as the only product. The reaction mixture was cooled to −78 °C, Me_2SiCl_2 (0.064 mol) was added, and after it was warmed to room temperature, the mixture was stirred for 5 h. The mixture was washed with aqueous HCl, evaporated to dryness, redissolved in 100 mL of THF, and added to 300 mL of MeOH to precipitate polymer **5a**, which was filtered and dried in vacuo (yield 94%).
(4) Ishikawa, M.; Hasegawa, Y.; Kunai, A. *J. Organomet. Chem.* **1990**, *381*, C57.
(5) The synthesis of **5b** has been claimed[6] to occur simply by heating $Ph_2Si(C{\equiv}CH)_2$. We have shown that the deep red polymer obtained is not **5b** but a highly cross-linked silylene–olefin polymer resulting from free-radical polymerization.[7]
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Registry No. (3)($ClMe_2(Si)_2Me_2Cl$) (copolymer), 129064-81-9; 4 (SRU), 128599-15-5; **5a** (copolymer),129102-13-2; **5a** (SRU), 128599-08-6; **5b** (copolymer),128359-14-8; **5b** (SRU), 31693-69-3; **5c** (copolymer),128359-08-0; **5c** (SRU), 128599-09-7; I_2, 7553-56-2; AsF_5, 7784-36-3; $FeCl_3$, 7705-08-0.