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# New Poly[(silylene)diacetylenes] and Poly[(germylene)diacetylenes]: Synthesis and Conductive Properties

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The reaction of dilithiobutadiyne (or the corresponding di-Grignard reagent) with various dichlorosilanes and dibromogermanes in THF at room temperature afforded poly[(silylene)diacetylenes] and poly[(germylene)diacetylenes], respectively, in high yields. The polymers have a regular alternating arrangement of diyne and silylene or germylene units. When they are doped with $FeCl_3$, these polymers show conductivity values in the range $10^{-5}$–$10^{-3}$ S·cm$^{-1}$. The values depend greatly on the electronic character of the substituents bonded to silicon or germanium.

## Introduction

In recent years, much attention has been paid to silicon-containing polymers as sources of novel materials in terms of their optical and electronic properties[1] or as precursors to ceramics by thermal decomposition.[2]

In this context, we were interested in investigating molecularly defined silylene and germylene polymers, $[-(ER_2)_mC{\equiv}C{-}C{\equiv}C-]_n$ with E = Si or Ge, containing a regular alternating arrangement of $(ER_2)_m$ and diyne units in the polymer backbone.[3]

Such derivatives would be of interest in order to explore the ability of a silicon or germanium atom inserted in a conjugated carbon backbone to allow charge-transport properties. In particular, silyl or polysilyl groups are known to be involved in conjugation with unsaturated groups either through a $(d{-}p)_\pi$ overlap[4] or a $(\sigma^*{-}p)_\pi$-type interaction.[5] Thus, the above molecules might be expected to exhibit properties consistent with a delocalization of the $\pi$-electron density along the main chain and to be candidates for conductive polymers.

**Table I**

$$C_4Li_2 + R^1R^2R^3EX \xrightarrow[0\ ^\circ C\text{ to room temp}]{THF} R^1R^2R^3EC{\equiv}C{-}C{\equiv}CER^1R^2R^3$$

| E | X | R¹ | R² | R³ | yield, % |
|---|---|---|---|---|---|
| Si | Cl | Et | Et | Et | 98 |
| | | Ph | Me | Me | 98 |
| | | Ph | Ph | Me | 94 |
| | | Ph | Ph | Ph | 85 |
| | | Me | Me | H | 84 |
| | | Ph | Ph | H | 91 |
| | | MeO | MeO | MeO | 45 |
| | | EtO | EtO | EtO | 57 |
| Ge | Br | Et | Et | Et | 76 |
| | | Me | Me | Ph | 60 |
| | | Me | Ph | Ph | 80 |
| Sn | Cl | Ph | Ph | Ph | 78 |

In this paper, we report our synthetic approach to new (silylene)- and (germylene)diacetylene polymers and their conducting properties. The possibility of modulating the charge-transport properties by the electronic effects of substituents grafted on the Si or Ge atom was investigated.

## Results and Discussion

**Preparation of the (Silylene)- and (Germylene)diacetylene Polymers.** Poly(silaacetylides) $[-SiR_2{-}C{\equiv}C-]_n$ have been prepared by reaction of $BrMgC{\equiv}CMgBr$, $Mg(C{\equiv}C)_n$, and $LiC{\equiv}CLi$ with dichlorosilanes.[6] Re-

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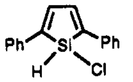
Table II

$$C_4Li_2\text{ (or }C_4Mg_2Br_2\text{)} + X[-R^1R^2E-]_mX \xrightarrow{\text{THF}} \xrightarrow{\text{MeOH}} [-(ER^1R^2E)_mC{\equiv}C{-}C{\equiv}C-]_n$$

$$E = Si,\ X = Cl,\ m = 1, 2;\ E = Ge,\ X = Br,\ m = 1$$

| chlorosilane | polymer[f] | yield, % | $M_w$[b] | $M_w/M_n$ | $n_w$ | mp, °C | $T_g$, °C[e] |
|---|---|---|---|---|---|---|---|
| $Me_2SiCl_2$ | **1** | 100 | 4060 | 1.24 | 38 | 150 | 27 |
| $Et_2SiCl_2$ | **2** | 100 | 6070 | 1.45 | 45 | 170–190 | |
| $Cl(Me_2Si)_2Cl$[a] | **3** | 100 | 3540 | 1.41 | 21 | 160 | |
| $MePhSiCl_2$ | **4** | 95 | 3070 | 1.64 | 18 | 80–110 | 25 |
| $Ph_2SiCl_2$ | **5** | 97 | 1830 | 1.31 | 8 | 210 dec | |
| $Me(p\text{-}MeC_6H_4)SiCl_2$ | **6** | 87 | 2710 | 1.30 | 15 | 90–130 | |
| $Me(p\text{-}MeOC_6H_4)SiCl_2$ | **7** | 91 | 1822 | 1.24 | 9 | 90–120 | |
| $CH_2{=}CH(Me)SiCl_2$[a] | **8** | 77 | 8830 | 1.99 | 75 | gum | 22 |
|  | **9** | 96 | 3330 | 1.96 | 12 | 96 | |
| $PhHSiCl_2$[a] | **10** | 87 | 4110 | 1.95 | 27 | 80 | |
| $(Me_3Si)_2SiCl_2$ | **11** | 85 | 7310 | 1.18 | 33 | *d* | |
| dibromogermane | polymer[f] | yield, % | $M_w$[b] | $M_w/M_n$ | $n_w$ | mp, °C[c] | $T_g$, °C[e] |
| $Ph_2GeBr_2$ | **12** | 87 | 2255 | 1.34 | 8 | 143–150 | 97 |
| $MePhGeBr_2$ | **13** | 79 | 3093 | 1.57 | 15 | 75–80 | 65 |
| $EtPhGeBr_2$ | **14** | 65 | 2522 | 1.34 | 11 | 105–110 | |
| $Et_2GeBr_2$ | **15** | 50 | 2401 | 1.85 | 13 | 130–140 | 75 |

[a] $C_4(MgBr)_2$ was used instead of $C_4Li_2$. [b] Weight-average molecular weights are determined relative to polystyrene standards. [c] The polymers visually appeared to melt and decompose in the range of temperatures indicated. [d] Infusible solid. [e] Measured with a torsion pendulum, except **13** and **15**, which were determined by DSC. [f] All of the polymers are soluble in the usual organic solvents such as benzene, THF, $CHCl_3$, and $CH_2Cl_2$.

cently, Barton et al. reported a more efficient access to these compounds, using a dilithioacetylide prepared by the reaction of trichloroethylene with *n*-butyllithium.[7] Poly(disilyleneethynylenes) have been also reported by Ishikawa[8] and West.[5f] In the case of polymers containing one germanium and acetylene units, one brief communication appeared in the late 1960s concerning $[-GePh_2-C{\equiv}C-C_6H_4C{\equiv}C-]_n$.[9]

In contrast, analogous polymers containing a diacetylene unit have been less explored. Previous attempts to prepare (silylene)diacetylene derivatives either by a copper-catalyzed oxidative coupling reaction[10] or by thermal polymerization[11] of $R_2Si(C{\equiv}CH)_2$ have failed to produce the expected compounds.[12] Concurrent with our studies,[2] Ishikawa et al. have reported the synthesis of two bis(silylene)diacetylene polymers $[-(ER^1R^2)_mC{\equiv}C-C{\equiv}C-]_n$ (E = Si, $m$ = 2; $R^1$ = Me, $R^2$ = Et, $R^1$ = Me, $R^2$ = Ph) by the reaction of $Li_2C_4$ with $(MeEtSiCl)_2$ and $(MePhSiCl)_2$.[13] Furthermore, preliminary data on the preparation of (silylene)diacetylene polymers by the reaction of dichlorosilanes and a dilithiobutadiyne obtained from *n*-butyllithium-induced dechlorination of hexachlorobutadiene were reported quite recently.[14]

According to the method previously reported by Walton et al. for the preparation of $Me_3SiC{\equiv}C-C{\equiv}CLi$,[15] the double-desilylation reaction of 1,4-bis(trimethylsilyl)butadiyne[16] with 2 equiv of the MeLi—LiBr complex (eq 1)

$$Me_3SiC{\equiv}C-C{\equiv}CSiMe_3 + 2MeLi{-}LiBr \xrightarrow[\text{room temp}]{\text{THF}} LiC{\equiv}C-C{\equiv}CLi + Me_4Si \quad (1)$$

afforded the expected dilithiobutadiyne in high yield. The di-Grignard reagent $C_4(MgBr)_2$ was obtained from $C_4Li_2$ by metal–metal exchange using $MgBr_2$ (eq 2). In order

$$LiC{\equiv}C-C{\equiv}CLi + 2MgBr_2 \xrightarrow[\text{room temp}]{\text{THF}} BrMgC{\equiv}C-C{\equiv}CMgBr \quad (2)$$

to assess the potential utility of the dilithio derivative, we carried out condensation by slow addition of the required amount of a monochlorosilane or monobromogermane. Various 1,4-bis(silyl)- and 1,4-bis(germyl)diacetylenes, some of them containing H or functional groups attached at the silicon atom, were obtained in high yields as shown in Table I. The dilithio derivative reacted also with $Ph_3SnCl$ to give the expected bis(triphenylstannyl)diacetylene derivative. The monodesilylation of 1,4-bis(trimethylsilyl)butadiyne using MeLi—LiBr has been previously reported,[15] and we used this method to prepare mixed silicon, germanium, or tin derivatives (Scheme I).

**Scheme I**

$$Me_3SiC{\equiv}C-C{\equiv}CSiMe_3 + \underset{1\text{ equiv}}{MeLi{-}LiBr} \xrightarrow{\text{THF}}$$

$$Me_3SiC{\equiv}C-C{\equiv}C^-Li^+ \xrightarrow{R_3EBr} Me_3SiC{\equiv}C-C{\equiv}CER_3$$

$ER_3$ = $GeEt_3$, 55%
$ER_3$ = $GePhMe_2$, 65%
$ER_3$ = $SnPh_3$, 78%

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**Table III. Physical Properties of the Silyl Polymers**

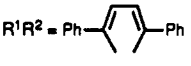
| $[-(SiR^1R^2)C_4-]_n$ | IR $\nu$(C≡C), $cm^{-1}$ $cm^{-1}$ | $^1$H NMR ($CCl_4$), $\delta$, ppm | $^{29}$Si NMR ($CDCl_3$), $\delta$, ppm | $^{13}$C NMR ($CDCl_3$), $\delta$, ppm |
|---|---|---|---|---|
| $R^1 = R^2 = Me$ | 2070, 2047 | 0.3 ($SiCH_3$) | −38.89 | −0.1 ($SiCH_3$); 82.3 (Si*C*≡C); 89.34 (SiC≡*C*) |
| $R^1 = R^2 = Et$ | 2070, 2042 | 0.6 (q, 2 H, $CH_2$); 0.87 (t, 3 H, $CH_3$) | −28.66 | 6.25 ($CH_2$); 7.37 ($CH_3$); 80.65 (Si*C*≡C); 90.02 (SiC≡*C*) |
| $R^1 = R^2 = Ph$ | 2075, 2050 | 3.58 ($CH_3$, chain end); 7–8 (m, Ph) | −47.37 | 52.3 ($CH_3O$, chain end); 80.54 (Si*C*≡C); 91.78 (SiC≡*C*); 128.8, 131.46, 136.37 (Ph) |
| $R^1 = Me$; $R^2 = Ph$ | 2070, 2050 | 0.46 (s, 3 H, $CH_3$); 7–8 (m, 5 H, Ph) | −42.14 | −0.66 ($CH_3$); 81.42 (Si*C*≡C); 90.63 (SiC≡*C*); 128.7, 131.12, 134.5 (Ph) |
| $R^1 = Me$; $R^2 =$ *p*-$MeC_6H_4$ | 2070, 2047 | 0.47 (s, 3 H, $SiCH_3$); 2.37 (s, 3 H, $CH_3$); 7–8 (AA′BB′ system, 4 H, Ph) | −42.11 | −0.55 ($SiCH_3$); 22.07 ($CH_3$); 52.3 ($CH_3O$, chain end), 81.63 (Si*C*≡C); 90.57 (SiC≡*C*); 129.35, 129.58, 134.04, 134.59, 141.47 (Ph) |
| $R^1 = Me$; $R^2 =$ *p*-$MeOC_6H_4$ | 2070, 2047 | 0.46 (s, 3 H, $CH_3$); 3.66 (s, 3 H, $OCH_3$); 7.21 (AA′BB′ system, 4 H, Ph); 0.32 ($SiCH_3$, chain end) | −42.42 | −0.47 ($SiCH_3$); 52.0 ($OCH_3$ chain end); 55.49 (*p*-$CH_3O$); 81.75 (Si*C*≡C); 90.46 (SiC≡*C*); 114.55, 122.50, 136.19, 162.21 ($-C_6H_4-$) |
| $R^1 = Me$; $R^2 =$ vinyl | 2070, 2049 | 0.26 (s, 3 H, $CH_3$); 5.75 (s, 3 H, vinyl) | −44.33 | −1.45 ($CH_3$); 80.85 (Si*C*≡C); 90.02 (SiC≡*C*); 131.02, 137.49 ($CH_2$=CH) |
| $R^1 = H$; $R^2 = Ph$ | 2076, 2049 | 4.87 (s, 1 H, SiH); 7–8 (m, 5 H, Ph) | −62.29 (d, $J_{SiH}$ = 241 Hz) | 78.28 (Si*C*≡C); 91.38 (SiC≡*C*); 125.63, 128.41, 131.92 (Ph) |
|  | 2070, 2043 | 7–8 (m, Ph and =CH); 0.32 ($SiMe_3$, chain end) | −15.43 | 86.35 (Si*C*≡C); 88.87 (SiC≡*C*); 127.53, 129.09 (Ph); 138.7, 141.2 (C=CH) |
| $(SiR^1R^2) = -(SiMe_2)_2-$ | 2060, 2039 | 0.26 (s, $CH_3$) | −35.47 | −3.00 ($SiCH_3$); 84.66 (Si*C*≡C); 91.19 (SiC≡*C*) |
| $R^1 = R^2 = SiMe_3$ | 2080, 2060 | 0.21 (s, $CH_3$) | | −1.68 (SiMe); 88.34 (Si*C*≡C); 92.94 (SiC≡*C*) |

**Table IV. Physical Properties of the Germyl Polymers**

| $[-GeR^1R^2C_4-]_n$ | IR ($CCl_4$) $\nu$(C≡C), $cm^{-1}$ | $^1$H NMR ($CCl_4$), $\delta$, ppm | $^{13}$C NMR ($CDCl_3$), $\delta$, ppm |
|---|---|---|---|
| $R^1 = R^2 = Ph$ | 2074 | 7.0–7.6 (m, Ph) | 79.3 (Ge*C*≡C); 90.3 (GeC≡*C*); 128.9, 129.2, 130.0, 130.9, 132.4, 134.2 (GePh) |
| $R^1 = Me$; $R^2 = Ph$ | 2073 | 0.45 (s, GeMe, chain end); 0.66 (s, GeMe); 7.1–7.6 (GePh) | −0.9 (GeMe, chain end); 0.2 (GeMe); 80.38 (Ge*C*≡C); 89.32 (GeC≡*C*); 128.74, 129.1, 129.71, 130.7, 133.46 (GePh) |
| $R^1 = Et$; $R^2 = Ph$ | 2071 | 0.40 (s, GeMe, chain end); 0.9–1.4 (m, 5 H, Et); 7.0–7.7 (m, 5 H, Ph) | −3.3 (GeMe, chain end); 8.82, 9.20, 10.48 (GeEt);[a] 79.42 (Ge*C*≡C); 89.87 (GeC≡*C*); 128.05, 129.6, 130.6, 132.74, 133.8 (GePh) |
| $R^1 = R^2 = Et$ | 2068 | 0.13 (s, GeMe, chain end) | 7.81 ($GeCH_2$); 8.97 ($GeCH_3$); 79.87 (Ge*C*≡C); 89.34 (GeC≡*C*) |

The condensation of $C_4Li_2$[17] or $C_4(MgBr)_2$ with various dichlorosilanes was carried out in THF. The reactions were performed with a slight excess of dichlorosilane in order to favor the formation of silicon–chlorine terminations; these species were quenched with MeOH to give methoxylated compounds. The desired polymers were obtained in excellent yields, as indicated in Table II.

The reaction took place readily under mild conditions (see Experimental Section for details). Various side groups such as trimethylsilyl groups (Table II, compound 11) or aromatic rings with electron-donating groups (Me, OMe; Table II, compounds 6 and 7) have been introduced as substituents at silicon. In the case of vinylmethyldichlorosilane, the di-Grignard reagent was used instead of the dilithio derivative in order to avoid the addition on the double bond[18] and, thus, side cross-linking reactions. The polycondensation reactions with dichlorotetramethyldisilane and phenyldichlorosilane were also performed with the di-Grignard reagent to prevent the cleavage of the Si–Si or Si–H bond, respectively. The coupling reaction with 1-chloro-2,5-diphenylsilacyclopentadiene resulted in the displacement of both exocyclic bonds.

With the germanium derivatives, the dibromides, which are more reactive and more easily prepared, were used instead of the dichloride compounds. The condensation procedure was the same as for the silicon compounds, but the germanium derivatives with alkyl and aryl substituents were ended with a methyl group, using methylmagnesium bromide as the quenching agent.

Weight-average molecular weights in the range of $M_w$ = 1800–4000 relative to polystyrene standards were determined by gel permeation chromatography (GPC) (Table II). A weight-average molecular weight of 6070 in the case of poly[(diethylsilylene)diacetylene] corresponds to a polymerization degree of about $n_w$ = 45 (45 (silylene)diacetylene units on average). A total of 38 units have been found in the case of the corresponding dimethylated polymer. Changing the alkyl substituents to aryl groups results in a significant decrease of the polymerization degree, and $n_w$ is only 8 in the case of poly[(diphenylsilylene)diacetylene]. This may be due to both steric hindrance and electronic factors lowering the rate of the polymerization process. The longest chain was obtained in the case of the methylvinylsilyl derivative ($n_w$ = 75 units) with a polydispersity of 1.99 ($M_w/M_n$ from GPC). Interestingly, the polydispersity values are low, in the range of 1.2–2.0 (Table I), and are consistent with purely linear structures for all of the described polymers. The same observations can be made in the case of the germanium derivatives (Table II), except that the yields are lower and that a decrease of the polymerization degree is observed, i.e., $n_w$ = 8–14 only.

The polymers were characterized by using IR, UV, and

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[17] $C_4Li_2$ can be also prepared by lithiation of (*Z*)-1-methoxybut-1-en-3-yne according to the method described in ref 16. However, polymers of lower molecular weights are generally obtained from reactions with dichlorosilanes when this method is used to produce $C_4Li_2$[3]. This is certainly partly due to the presence of the reactive MeOLi. The latter will convert the initial chlorosilanes into less reactive methoxysilanes. MeOLi is also able to cleave the labile Si–$C_{sp}$ bonds present in the final products.

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**Table V. Conductivity Values for the Poly[(silylene)diacetylenes] and Their Germanium Analogues**

| polymer[a] | conductivity, S·cm$^{-1}$ [b] |
|---|---|
| $[-Me_2SiC_4-]_n$ (1) | $8 \times 10^{-5}$ |
| $[-(Me_2Si)_2C_4-]_n$ (3) | $5 \times 10^{-5}$ |
| $[-MePhSiC_4-]_n$ (4) | $10^{-4}$ |
| $[-Ph_2SiC_4-]_n$ (5) | $3 \times 10^{-3}$ |
| $[-Me(p\text{-}MeC_6H_4)SiC_4-]_n$ (6) | $2 \times 10^{-4}$ |
| $[-Me(p\text{-}MeC_6H_4)SiC_4-]_n$ (7) | $3 \times 10^{-4}$ |
| $[-Ph_2GeC_4-]_n$ (12) | $10^{-4}$ |
| $[-MePhGeC_4-]_n$ (13) | $3 \times 10^{-5}$ |
| $[-EtPhGeC_4-]_n$ (14) | $2 \times 10^{-5}$ |

[a] In their undoped state, the polymers are insulators; conductivity values range from $10^{-12}$ to $10^{-13}$ S·cm$^{-1}$. [b] Upon doping with $FeCl_3$.

liquid NMR spectroscopy. The $^1H$, $^{13}C$, and $^{29}Si$ NMR spectra of all the compounds are consistent with the assigned structure of the polymer chain. These values are summarized in Tables III and IV.

As an example, the IR spectrum of poly[(dimethylsilylene)diacetylene] exhibits a strong band at 2073 cm$^{-1}$ ($\nu$(C≡C)). The $^{13}C$ NMR spectrum shows signals centered at 0.1 ppm and at 82.3 and 89.3 ppm (relative to TMS) due to the methyl and ethynylic carbons, respectively. Furthermore, the $^{29}Si$ NMR spectrum is also in agreement with a silicon atom bearing ethynyl groups with a singlet at −36.89 ppm.[19]

All of the polymers, except poly[(methylvinylsilylene)diacetylene], are cream to brown powders. They are soluble in a variety of the usual organic solvents, such as benzene, THF, chloroform, and dichloromethane. They visually appear to melt between 100 and 200 °C (Table II) according to the nature of the substituents attached at silicon. Indeed, the differential scanning calorimetry (DSC) curves of the above polymers showed no distinct melting endotherms. The glass transition temperatures ($T_g$) were obtained for polymers **13** and **15**. In the case of polymers **1**, **4**, **8**, and **12** the $T_g$ values were determined using a torsion pendulum. We have also to outline their particular thermal stability. In contrast to the usual polyynes, which are unstable,[20] we observe no degradation reaction below 150 °C.

**Conductivity Study.**[21] Some of the prepared polymers have been cast as thin films on a glass substrate from their methylene chloride solutions and the conductivities determined by the four-probe method.[22] All the films are insulators, with conductivity values ranging from $10^{-12}$ to $10^{-15}$ S·cm$^{-1}$. The doping of these polymers has been carried out by the use of an electron acceptor such as $FeCl_3$ in a dichloromethane solution (see the Experimental Section for details). The doping reaction with $FeCl_3$ follows the procedure classically used in the field of organic conjugated polymers, such as polyacetylene, polypyrrole, and polythiophene, which are switched from their neutral insulating state to a doped conducting one by the use of a chemical oxidant. The appropriate amount of $FeCl_3$ is determined by the number of unsaturated bonds per monomeric unit in the polymer and by the fact that 2 mol of $FeCl_3$ is necessary to obtain 1 mol of $FeCl_4^-$ ($2FeCl_3 \rightarrow FeCl_4^- + FeCl_2$). As in the case of the well-described conjugated polymers, this doping reaction is reversible, the neutral state being obtained by the use of a reducing species such as an amine or even by washing the doped polymer with a solvent able to remove the $FeCl_4^-$ ions. This undoping reaction has also been realized in the present case for poly[(silylene or germylene)diacetylenes], and the undoped material obtained shows the same IR absorption spectrum as the starting polymer.[23]

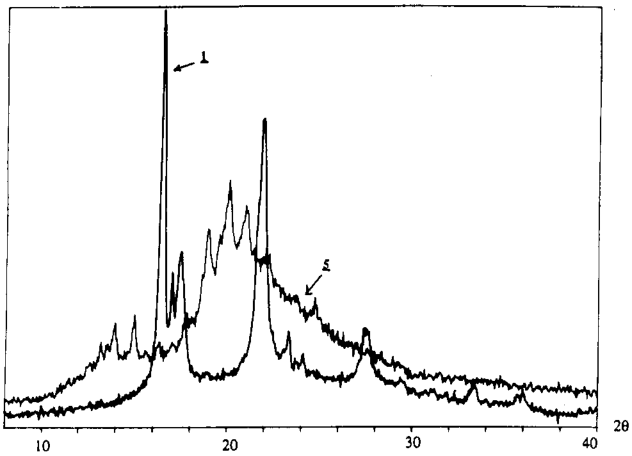

**Figure 1.** X-ray powder diffraction patterns for **1** and **5**.

The conductivities of the doped polymers have been measured, and the data are summarized in Table V.

Upon doping with $FeCl_3$, the conductivity reaches $10^{-5}$–$10^{-3}$ S·cm$^{-1}$; these relatively high values are comparable to those obtained for fully conjugated organic polymers.[24] As observed also by others for different conjugated silicon-containing polymers,[1] the data show that the intercalation of a silicon atom in a conjugated polymeric carbon backbone still allows the transfer of the charges. The presence of two consecutive silicon atoms does not prevent conductivity in the polymer.

The replacement of a methyl group in the polymer **1** by a phenyl group (Table IV, polymer **3**) enhances the conductivity of the doped polymer. Furthermore, an electron-donating group (Me or MeO) attached at the para position of the phenyl group (Table V, **4**, **6**, **7**) significantly increases the conductivity, which reaches $3 \times 10^{-4}$ S·cm$^{-1}$ in the case of poly[(methyl(*p*-methoxyphenyl)silylene)diacetylene] (**7**). These data clearly outline the possibility of modulating the charge-transport properties by electronic effects of substituents grafted on the silicon atom. The aryl groups, which are able to stabilize a positive charge, lead to relatively high conductivity values. Furthermore, poly[(dimethylsilylene)diacetylene] (**1**), for which we may expect the shortest interchain distances, exhibits a 50 times lower conductivity. The X-ray powder diffraction pattern for **1** is indicative of a partially crystalline structure (Figure 1). The repeat distance of the diacetylene backbone inside this region was measured as 4.6 Å. In contrast, poly[(diphenylsilylene)diacetylene] (**5**), for which a higher conductivity value was obtained (Table V), exhibits a significantly lower degree of crystallinity (Figure 1). The interchain distance was found to be about 6 Å. This seems to be in agreement with a charge transport occurring mainly along the main chain of the polymer through the silicon atoms. Finally, the influence of the hetero element

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(23) No chemical reaction was observed between **1** and $FeCl_3$. Indeed, a solution of $FeCl_3{\cdot}6H_2O$ (0.25 M; 4 mL, 0.001 mol) in THF was added to the polymer **1** (0.106 g, 0.001 mol) dissolved in 20 mL of THF and the mixture was stirred at room temperature for 15 h. The solvent was then removed under vacuum, and the residue was washed with 10 mL of $CH_3NO_2$ to remove $FeCl_3$. Polymer **1** was recovered quantitatively.

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on the conducting properties was studied by exchanging germanium for silicon. The polymers obtained (Table V, polymers 12–14), doped with $FeCl_3$ under the same conditions as for the silicon polymers, gave slightly lower conductivity values than their silicon analogues. Due to the fact that the electronegativities and bond lengths are not very different between silicon and germanium, conducting values on the same order of magnitude should be expected.

## Conclusion

The polymers prepared in this study are insulators, but conductivity values reach $10^{-5}$–$10^{-3}$ S·cm$^{-1}$ when they are doped with $FeCl_3$. The conductivities depend on the electronic effects of the groups attached at the silicon or germanium atom. When we take into account the ease of functionalization provided by the silicon or germanium atom and the particular stability of this class of polymers, they appear very promising for the design of new functionalized electrically conducting polymers.

## Experimental Section

All reactions were carried out under argon or nitrogen using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. Tetrahydrofuran (THF) was first distilled over calcium hydride and then over sodium benzophenone.

The mono- and dichlorosilanes used were purchased from Janssen, Aldrich, or Lancaster and distilled over magnesium before use. Triphenyltin chloride was purchased from Aldrich, methyllithium–lithium bromide solution in ether from Aldrich, *n*-BuLi in hexane from Janssen. 1-Methoxy-1-buten-3-yne from Aldrich was purified according to the literature.[25] The following derivatives were prepared according to published methods: 1,4-bis(trimethylsilyl)-1,3-butadiyne,[16] chlorotrimethoxy- and chlorotriethoxysilanes,[26] 1,2-dichlorotetramethyldisilane,[27] dichloromethyl-*p*-tolylsilane and dichloromethyl-*p*-anisylsilane,[28] and bis(trimethylsilyl)dichlorosilane.[29] Triethylbromogermane, dimethylphenylbromogermane, diphenylmethylbromogermane, triphenylbromogermane, diphenyldibromogermane, methylphenyldibromogermane, and ethylphenyldibromogermane were prepared from germanium tetrachloride using the general procedure of Brook and Peddle.[30] Diethyldibromogermane was prepared according to Mazerolles.[31] $MgBr_2$ was prepared from magnesium and 1,2-dibromoethane in THF as solvent followed by the evaporation of the volatiles.

$^1$H NMR spectra were obtained on a Bruker AW-60, AW-80, or AC-250 instrument and $^{13}$C and $^{29}$Si NMR spectra on a Bruker AC-200 or AC-250 spectrometer; the chemical shifts, $\delta$, are relative to tetramethylsilane (TMS). IR spectra were recorded on a Perkin-Elmer 298 or 1600 spectrometer and mass spectra on a JEOL JMS-D 100 instrument.

Gas permeation chromatography (GPC) was performed using a Waters 410 instrument with UV and refractive index detection. The solvent used was THF, and the porosities of the columns used were 100, 500, $10^3$, and $10^4$ Å. The elution rate was 0.9 mL min$^{-1}$. Melting points were taken using a Gallenkamp melting point apparatus and are uncorrected.

X-ray diffraction measurements were obtained using Cu K$\alpha$ radiation with a Philips diffractometer interfaced with a multiacquisition computerized system developed by Prof. R. Fourcade (Université de Montpellier II).

$T_g$ measurements were performed by Rhône-Poulenc using a homemade torsion pendulum or a DSC Mettler 30 instrument.

**Synthesis of the 1,3-Butadiyne Compounds.** In these reactions, 1,4-dilithio-1,3-butadiyne was prepared by starting from 1-methoxy-1-buten-3-yne according to the Zweifel procedure.[16]

**1,4-Bis(triethylsilyl)-1,3-butadiyne.** The following procedure is given as an example. Chlorotriethylsilane (0.052 mol, 8.7 mL) was added neat to a slurry of 1,4-dilithio-1,3-butadiyne (0.025 mol) prepared in THF as solvent. The reaction mixture was stirred at room temperature for 2 h. After hydrolysis using a saturated solution of $NH_4Cl$ and extraction with pentane, the organic phase was concentred under vacuum. Further purification using column chromatography ($SiO_2$, pentane as eluent) gave 6.9 g (0.0248 mol, 98% yield) of the title compound. The physical properties are identical with those reported in the literature.[20]

**1,4-Bis(dimethylphenylsilyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(triethylsilyl)-1,3-butadiyne was used, with 0.015 mol of the dilithio reagent and 0.032 mol (5.5 mL) of chlorodimethylphenylsilane; 6.67 g (98% yield) of the title compound was obtained. Mp: 63–64 °C. $^1$H NMR ($CCl_4$; $\delta$, ppm): 0.33 (s, 6 H, $CH_3$), 7–8 (m, 5 H, Ph). $^{13}$C NMR ($CDCl_3$; $\delta$, ppm): −0.86 (Si$C$H$_3$), 84.90 (Si$C$≡C), 89.98 (SiC≡$C$), 135.09, 135.93, 134.16, 130.24, 128.48 (Ph). $^{29}$Si NMR ($CDCl_3$; $\delta$, ppm): −20.27. Anal. Calcd for $C_{20}H_{22}Si_2$: C, 75.47; H, 6.92. Found: C, 75.15; H, 6.87.

**1,4-Bis(methyldiphenylsilyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(triethylsilyl)-1,3-butadiyne was used with 0.015 mol of the dilithio reagent and 0.032 mol (7 mL) of methyldiphenylchlorosilane. Recrystallization from hexane gave 6.24 g (94% yield) of the title compound as a white solid. Mp: 142 °C. $^1$H NMR ($CCl_4$; $\delta$, ppm): 0.46 (s, 3 H, $CH_3$), 7–8 (m, 10 H, Ph). $^{13}$C NMR ($CDCl_3$; $\delta$, ppm): −1.83 (Si$C$H$_3$), 83.77 (Si$C$≡C), 91.43 (SiC≡$C$), 135.09, 134.34, 130.59, 128.63, (Ph). $^{29}$Si ($CDCl_3$; $\delta$, ppm): −24.42. IR ($CCl_4$; cm$^{-1}$): $\nu$(CH) 3071, 2965; $\nu$(C≡C) 2070, 2047; $\delta$(SiPh) 1429, 1115; $\delta$(SiMe) 1250. Mass spectrum (IE; *m/e* (relative intensity)): 442 ($M^+$ 33), 427 ($M^+$ − Me, 32), 197 ($SiPh_2Me^+$, 100). Anal. Calcd for $C_{30}H_{26}Si_2$: C, 81.45; H, 5.88. Found: C, 81.20; H, 6.14.

**1,4-Bis(triphenylsilyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(triethylsilyl)-1,3-butadiyne was used, with 0.01 mol of the dilithio reagent and 0.02 mol (5.89 g) of triphenylchlorosilane dissolved in 10 mL of THF. Recrystallization from carbon tetrachloride gave 4.83 g (85% yield) of the title compound as a white solid. Mp: 304 °C. $^1$H NMR ($CCl_4$; $\delta$, ppm): 7–8 (m, Ph). IR ($CCl_4$; cm$^{-1}$): $\nu$(CH) 3068, 3008; $\nu$(C≡C) 2070, 2047; $\delta$(SiPh) 1482, 1429, 1111. Mass spectrum (IE; *m/e*): 566 ($M^+$), 488 ($M^+$ − Ph), 259 ($SiPh_3^+$). Anal. Calcd for $C_{40}H_{30}Si_2$: C, 84.80; H, 5.30. Found: C, 84.30; H, 4.99.

**1,4-Bis(dimethylsilyl)-1,3-butadiyne.** A slurry of 1,4-dilithio-1,3-butadiyne (0.05 mol) in THF was added slowly via a cannula to a solution of chlorodimethylsilane (0.015 mol, 16.6 mL) in THF (40 mL) cooled to 0 °C. The mixture was stirred at room temperature for 2 h, hydrolyzed using a saturated solution of $NH_4Cl$, and extracted several times with pentane. The organic phase was dried over $MgSO_4$ and concentrated under vacuum. Distillation gave the title compound: 7.0 g, 84% yield. Bp$_{18}$: 80 °C. $^1$H NMR ($CCl_4$; $\delta$, ppm): 0.26 (d, $J$ = 7 Hz, 6 H, $CH_3$), 4.1 (hept, $J$ = 7 Hz, 1 H, SiH). $^{29}$Si NMR ($CDCl_3$; $\delta$, ppm): −35.99 (d of hept, $J_1$ = 206 Hz, $J_2$ = 7.5 Hz). IR ($CCl_4$; cm$^{-1}$): $\nu$(CH) 2965; $\nu$(SiH) 2159; $\nu$(C≡C) 2073, 2050; $\delta$(SiMe) 1407, 1250. Anal. Calcd for $C_8H_{14}Si_2$: C, 57.83; H, 8.43. Found: C, 58.08; H, 8.45.

**1,4-Bis(diphenylsilyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(dimethylsilyl)-1,3-butadiyne was used, with 0.05 mol of the dilithio reagent and 0.015 mol (28.4 mL) of chlorodiphenylsilane in 40 mL of THF. Recrystallization from hexane gave 18.84 g (91% yield) of the title compound. Mp: 76–77 °C. $^1$H NMR ($CCl_4$; $\delta$, ppm): 5.14 (s, 1 H, SiH), 7–8 (m, 10 H, Ph). $^{13}$C NMR ($CDCl_3$; $\delta$, ppm): 81.22 (Si$C$≡C), 92.36 (SiC≡$C$), 135.78, 134.85, 131.09, 128.86 (phenyl group). $^{29}$Si NMR ($CDCl_3$; $\delta$, ppm): −39.64 (d, $J$ = 218 Hz). IR ($CCl_4$; cm$^{-1}$): $\nu$(CH) 3045; $\nu$(SiH) 2143; $\nu$(C≡C) 2065, 2047; $\delta$(SiPh) 1424, 1109. Mass spectrum (EI; *m/e* (relative intensity)): 413 ($M^+$ − 1, 100). Anal. Calcd for $C_{28}H_{22}Si_2$: C, 81.16; H, 5.31. Found: C, 80.81; H, 5.80.

**1,4-Bis(trimethoxysilyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(triethylsilyl)-1,3-butadiyne was used, with 0.015 mol of the dilithio reagent and 0.035 mol (5.5 mL) of chlorotrimethoxysilane. The mixture was stirred for 6 h at room temperature

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and concentrated under vacuum. The residue was extracted with 50 mL of hexane to remove the salts and the extract distilled to give 2.34 g (45% yield) of the title compound. Bp$_{0.8}$: 83 °C. $^1$H NMR (CCl$_4$; δ, ppm): 3.47 (s, CH$_3$). $^{13}$C NMR (CDCl$_3$; δ, ppm): 51.28 (OCH$_3$), 76.59 (Si*C*≡C), 86.87 (SiC≡*C*). $^{29}$Si NMR (CDCl$_3$; δ, ppm): −72.33. IR (CCl$_4$; cm$^{-1}$): ν(CH) 2937, 2838; ν(C≡C) 2080, 2060; δ(SiOCH$_3$) 1090, 1184. Anal. Calcd for $C_{10}H_{18}O_6Si_2$: C, 41.37; H, 6.21; Si, 19.31. Found: C, 41.14; H, 6.19; Si, 19.83.

**1,4-Bis(triethoxysilyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(trimethoxysilyl)-1,3-butadiyne was used, with 0.015 mol of the dilithio reagent and 0.035 mol (7 g) of chlorotriethoxysilane. Distillation gave 3.2 g (57% yield) of the title compound. Bp$_{0.05}$: 112 °C. $^1$H NMR (CCl$_4$; δ, ppm): 1.17 (t, $J$ = 7 Hz, 9 H, CH$_3$), 3.83 (q, $J$ = 7 Hz, 6 H, CH$_2$). $^{13}$C NMR (CDCl$_3$; δ, ppm): 18.29 (CH$_3$), 59.64 (OCH$_2$), 77.79 (Si*C*≡C), 86.47 (SiC≡*C*). $^{29}$Si (CDCl$_3$; δ, ppm): −75.88. IR (CCl$_4$; cm$^{-1}$): ν(CH) 2977, 2927, 2894; ν(C≡C) 2080, 2060; δ(SiOEt) 1168, 1103, 1080.

**1,4-Bis(triethylgermyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(triethylsilyl)-1,3-butadiyne was used, with 0.0072 mol of the dilithio reagent and 0.019 mol (4 mL) of bromotriethylgermane. The mixture was stirred at room temperature for 6 h and hydrolyzed with a saturated solution of NH$_4$Cl. Extraction with pentane followed by drying over MgSO$_4$ and distillation with a Kugelrohr apparatus gave 2 g (76% yield) of the title compound. Bp$_{0.01}$: 55 °C. $^1$H NMR (CCl$_4$; δ, ppm): 0.5–1.8 (m, Et). $^{13}$C (CCl$_4$; (CDCl$_3$; δ, ppm): 6.8 and 9.28 (Et), 83.26 (Ge*C*≡C), 89.38 (GeC≡*C*). IR (CCl$_4$; cm$^{-1}$): ν(CH) 2961, 2930, 2910, 2873, 2830, 2736; ν(C≡C) 2059; δ(CH$_2$CH$_3$) 1458, 1427, 1379, 1228, 1023. UV (pentane; λ$_{max}$, nm): 231, 244, 256, 270. Mass spectrum (EI; $m/e$): 368 (M$^+$), 339 (M$^+$ − Et). Anal. Calcd for $C_{16}H_{30}Ge_2$: C, 52.27; H, 8.22; Ge, 39.5. Found: C, 51.45; H, 8.22; Ge, 42.3.

**1,4-Bis(dimethylphenylgermyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(triethylgermyl)-1,3-butadiyne was used, with 0.005 mol of the dilithio reagent and 0.01 mol of bromodimethylphenylgermane. Kugelrohr distillation (bp$_{0.01}$ 135 °C) gave 2.4 g (60% yield) of the title compound. Mp: 47–48 °C. $^1$H NMR (CCl$_4$; δ, ppm): 0.4 (s, 6 H, CH$_3$), 7–7.5 (m, 5 H, Ph). $^{13}$C NMR (CDCl$_3$; δ, ppm): −0.85 (GeMe), 84.4 (Ge*C*≡C), 89.0 (GeC≡*C*), 128.7, 129.6, 133.4, 137.9 (GePh). IR (CCl$_4$; cm$^{-1}$): ν(CH) 3072, 3050, 2985, 2913; ν(C≡C) 2066; δ(Ph) 1485, 1432; δ(CH$_3$) 1241; δ(GePh) 1095. Mass spectrum (EI; $m/e$): 408 (M$^+$), 393 (M$^+$ − Me), 181 (GeMe$_2$Ph$^+$). Anal. Calcd for $C_{20}H_{22}Ge_2$: C, 58.9; H, 5.43; Ge, 35.62. Found: C, 59.2; H, 5.24; Ge, 35.52.

**1,4-Bis(methyldiphenylgermyl)-1,3-butadiyne.** The same procedure as for 1,4-bis(triethylgermyl)-1,3-butadiyne was used, with 0.01 mol of the dilithio reagent and 0.021 mol of bromomethyldiphenylgermane. The crude compound was crystallized from dichloromethane–pentane (50:50) to give 4.25 g (80% yield) of the title compound. Mp: 135–136 °C. $^1$H NMR (CCl$_4$; δ, ppm): 0.65 (s, 3 H, CH$_3$), 7.1–7.6 (m, 10 H, Ph). $^{13}$C NMR (CDCl$_3$; δ, ppm): −1.96 (GeCH$_3$), 82.6 (Ge*C*≡C), 90.24 (GeC≡*C*), 128.8, 129.9, 134.1, 136.2 (GePh). IR (CCl$_4$; cm$^{-1}$): ν(CH) 3072, 3055, 3001, 2915; ν(C≡C) 2067; δ(Ph) 1485, 1432; δ(Me) 1243; δ(GePh) 1094. Mass spectrum (EI; $m/e$): 532 (M$^+$), 516 (M$^+$ − Me). Anal. Calcd for $C_{30}H_{26}Ge_2$: C, 67.76; H, 4.93. Found: C, 67.49; H, 4.88.

**1,4-Bis(triphenylstannyl)-1,3-butadiyne.** A solution of triphenyltin chloride (4.2 g, 0.012 mol) in THF (30 mL) was added to a slurry of the dilithio reagent (0.0058 mol) in the same solvent and the mixture stirred at room temperature for 5 h, during which time the product precipitated. After hydrolysis with a saturated solution of NH$_4$Cl and extraction with large amounts of chloroform to dissolve the title compound, the organic phase was dried over MgSO$_4$ and concentrated under vacuum. Recrystallization from chloroform–ether (50:50) gave white crystals of the title compound: 3.4 g, 78% yield. Mp: 190 °C dec. $^1$H NMR (C$_6$D$_6$; δ, ppm): 6.4–7.8 (m, Ph). $^{13}$C NMR (CDCl$_3$; δ, ppm): 82.79 (SnC≡*C*), 94.58 (Sn*C*≡C), 128.8, 129.3, 129.7, 130.01, 136.4, 136.8, 137.1, 137.5 (Ph). $^{119}$Sn (CDCl$_3$; δ, ppm): −151.26. IR (CCl$_4$, cm$^{-1}$): ν(CH) 3070, 3053, 3020; ν(C≡C) 2050; δ(Ph) 1481, 1430; δ(SnPh) 1076. Mass spectrum (EI; $m/e$): 748 (M$^+$), 671 (M$^+$ − Ph), 351 (Ph$_3$Sn$^+$). Anal. Calcd for $C_{40}H_{30}Sn_2$: C, 64.22; H, 4.04; Sn, 31.73. Found: C, 64.01; H, 4.09; Sn, 30.47.

**1-(Trimethylsilyl)-4-(dimethylphenylgermyl)-1,3-butadiyne.** A solution of bromodimethylphenylgermane (2.6 g, 0.010 mol) in Et$_2$O (10 mL) was added to a solution of 1-lithio-4-(trimethylsilyl)-1,3-butadiyne[15] (0.010 mol) and the mixture stirred at room temperature for 3 h. The reaction mixture was hydrolyzed with a saturated solution of NH$_4$Cl and extracted several times with pentane and the organic phase dried over MgSO$_4$. Evaporation of the volatiles under vacuum followed by Kugelrohr distillation gave the title compound: 1.95 g, 65% yield. Bp$_{0.1}$: 110 °C. $^1$H NMR (CCl$_4$; δ, ppm): 0.0 (s, 9 H, SiMe), 0.5 (s, 6 H, GeMe), 7–7.5 (m, 5 H, GePh). $^{13}$C NMR (CDCl$_3$; δ, ppm): −0.91, −0.05 (CH$_3$), 85.2, 85.55 (Ge*C*≡C)(Si*C*≡C), 88.5, 88.9 (GeC≡*C*)(SiC≡*C*), 128.7, 129.6, 133.5 (Ph). $^{29}$Si (CDCl$_3$; δ, ppm): −16.04. IR (CCl$_4$; cm$^{-1}$): ν(CH) 3072, 3055, 2963, 2912; ν(C≡C) 2067; δ(Ph) 1485, 1432; δ(Me) 14.11; δ(SiMe) 1252; ν(GePh) 1095. Mass spectrum (EI; $m/e$): 302 (M$^+$), 287 (M$^+$ − Me). Anal. Calcd for $C_{15}H_{20}SiGe$: C, 59.85; H, 6.69; Ge, 24.12; Si, 9.33. Found: C, 60.00; H, 6.63; Si, 9.36; Ge, 24.33.

**1-(Trimethylsilyl)-4-(triethylgermyl)-1,3-butadiyne.** The same procedure as for 1-(trimethylsilyl)-4-(dimethylphenylgermyl)-1,3-butadiyne was used, with bromotriethylgermane (0.01 mol, 2 mL) and 1-lithio-4-(trimethylsilyl)-1,3-butadiyne (0.01 mol) in Et$_2$O. Kugelrohr distillation gave 1.5 g (55% yield) of the title compound. Bp$_{0.5}$: 60 °C. $^1$H NMR (CCl$_4$; δ, ppm): 0.0 (s, 9 H, SiCH$_3$), 0.5–1.1 (m, 15 H, GeEt). $^{13}$C NMR (CDCl$_3$; δ, ppm): −0.01 (SiMe), 6.06 and 9.28 (GeEt), 83.6, 86.0 (Ge*C*≡C)(Si*C*≡C), 88.72, 89.08 (GeC≡*C*)(SiC≡*C*). $^{29}$Si NMR (CDCl$_3$; δ, ppm): −16.38. IR (CCl$_4$; cm$^{-1}$): ν(CH) 2059, 2932, 2907, 2874; ν(C≡C) 2064; δ(GeEt) 1458, 1426, 1380, 1023; δ(SiMe) 1252. Mass spectrum (EI; $m/e$): 282 (M$^+$), 267 (M$^+$ − CH$_3$), 253 (M$^+$ − Et), 225 (M$^+$ − 2Et). Anal. Calcd for $C_{13}H_{24}SiGe$: C, 55.59; H, 8.55; Ge, 25.87; Si, 9.97. Found: C, 55.82; H, 8.34; Ge, 25.04; Si, 9.84.

**1-(Trimethylsilyl)-4-(triphenylstannyl)-1,3-butadiyne.** The same procedure as for 1-(trimethylsilyl)-4-(dimethylphenylgermyl)-1,3-butadiyne was used, with bromotriphenylstannane (4.3 g, 0.01 mol) in 30 mL of Et$_2$O and 1-lithio-4-(trimethylsilyl)-1,3-butadiyne (0.01 mol) in Et$_2$O. White crystals of the title compound were obtained after recrystallization from diethyl ether–pentane (50:50): 3.67 g, 78% yield. Mp: 102–103 °C. $^1$H NMR (CCl$_4$; δ, ppm): 0.0 (s, 9 H, Me), 7–7.6 (m, 15 H, Ph). $^{13}$C (CDCl$_3$; δ, ppm): −0.02 (SiMe), 84.56 (Si*C*≡C and Sn*C*≡C), 88.7 (SiC≡*C*), 94.37 (SnC≡*C*), 128.6, 129.3, 129.7, 130.1, 136.3, 136.7, 137.1, 137.4 (SnPh). $^{29}$Si NMR (CDCl$_3$; δ, ppm): −15.9. IR (CCl$_4$; cm$^{-1}$): ν(CH) 3068, 3055, 2962, 2912; ν(C≡C) 2057; δ(Ph) 1482, 1430; δ(SiMe) 1252; ν(SnPh) 1076. Mass spectrum (EI; $m/e$): 473 (M$^+$), 458 (M$^+$ − CH$_3$). Anal. Calcd for $C_{25}H_{24}SiSn$: C, 63.71; H, 5.13; Si, 5.96; Sn, 25.19. Found: C, 63.8; H, 5.08; Si, 5.69; Sn, 24.48.

**Synthesis of the Poly[(silylene)diacetylene] Derivatives. 1,4-Dilithio-1,3-butadiyne.** This procedure is an extension of the desilylation reaction performed by Walton et al. to obtain 1-lithio-4-(trimethylsilyl)-1,3-butadiyne.[15]

A solution of MeLi—LiBr in diethyl ether (0.02 mol) was added dropwise to a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (1.94 g, 0.01 mol) in THF (60 mL). The dilithio derivative precipitated, and the reaction mixture was stirred at room temperature for 3 h. This slurry was used without other treatment.

**1,4-Bis(bromomagnesio)-1,3-butadiyne.** The prepared MgBr$_2$ (10 g, excess) was added portionwise to a slurry of 1,4-dilithio-1,3-butadiyne in THF (60 mL), and the reaction mixture was stirred at room temperature for 3 h. This slurry was used as prepared.

**General Procedure.** The dichlorosilane (0.012 mol) was added neat over 1 h, using an automatic syringe, to a slurry of 1,4-dilithio-1,3-butadiyne (0.01 mol) in THF (70 mL), and the mixture was stirred for 12 h. A 0.5-mL portion of methanol was then added to substitute the Si–Cl terminations, and the reaction mixture was stirred for 2 h. After hydrolysis using a cold saturated solution of NH$_4$Cl, the mixture was extracted several times with pentane. The organic phase was then dried over MgSO$_4$ and the solvent removed under vacuum to give a powder in quantitative yield.

**Poly[(dimethylsilylene)diacetylene] (1).** A cream-colored solid (1.05 g, quantitative yield) was obtained. See Tables II and III for physical properties. Anal. Calcd for $(C_6H_6Si)_n$: C, 66.03; H, 5.66; Si, 26.41. Found: C, 61.31; H, 5.91; Si, 22.90; O, 2.47.

**Poly[(diethylsilylene)diacetylene] (2).** The general procedure was used to give 1.34 g (quantitative yield) of a beige powder of 2. See Tables II and III for physical properties. Anal. Calcd for $(C_8H_{10}Si)_n$: C, 71.64; H, 7.46; Si, 20.89. Found: C, 67.01; H, 9.46; Si, 19.20; O, 0.83.

**Poly[(tetramethyldisilylene)diacetylene] (3).** The general procedure was used with 1,4-bis(bromomagnesio)-1,3-butadiyne and gave 1.64 g (quantitative yield) of a beige powder of 3. See Tables II and III for physical properties. UV (THF; $\lambda_{max}$, nm): 236, 257, 274, 291. Anal. Calcd for $(C_8H_{12}Si_2)_n$: C, 58.53; H, 7.32; Si, 34.14. Found: C, 55.88; H, 8.17; Si, 20.60; O, 1.76.

**Poly[(methylphenylsilylene)diacetylene] (4).** The general procedure was used and gave 1.6 g (95% yield) of a beige powder. See Tables II and III for physical properties. Anal. Calcd for $(C_{11}H_8Si)_n$: C, 78.57; H, 4.76; Si, 16.20. Found: C, 77.76; H, 5.01; Si, 15.80; O, 0.76.

**Poly[(diphenylsilylene)diacetylene] (5).** The general procedure was used and gave 2.23 g (97% yield) of the title compound as a cream-colored powder. See Tables II and III for physical properties. Anal. Calcd for $(C_{16}H_{10}Si)_n$: C, 84.47; H, 4.34; Si, 12.17. Found: C, 80.17; H, 4.32; Si, 12.20; O, 1.54.

**Poly[(*p*-tolylmethylsilylene)diacetylene] (6).** The general procedure was used and gave 1.6 g (87% yield) of the title compound as a beige powder. See Tables II and III for physical properties. Anal. Calcd for $(C_{12}H_{10}Si)_n$: C, 79.12; H, 5.49; Si, 15.38. Found: C, 74.78; H, 5.50; Si, 13.98.

**Poly[(*p*-anisylmethylsilylene)diacetylene] (7).** The general procedure was used and gave 1.8 g (91% yield) of the title compound as a beige powder. The methanolysis was performed at −40 °C. See Tables II and III for physical properties. Anal. Calcd for $(C_{12}H_{10}OSi)_n$: C, 72.72; H, 5.05; Si, 14.14; O, 8.00. Found: C, 71.59; H, 5.38; Si, 14.50; O, 9.76.

**Poly[(methylvinylsilylene)diacetylene] (8).** The general procedure was used with 1,4-bis(bromomagnesio)-1,3-butadiyne and gave a brown sticky solid after washing with methanol. A 0.91-g amount (77% yield) of the title compound was obtained. See Tables II and III for physical properties.

**Poly[((1,4-diphenylbutadiene-1,4-diyl)silylene)diacetylene] (9).** The general procedure was used with 0.0037 mol of the dilithio reagent in THF and 0.0037 mol of 1-chloro-2,5-diphenylsilacyclopentadiene dissolved in 10 mL of THF. The reaction mixture was treated first with 0.5 mL of trimethylchlorosilane to quench the acetylide terminations and then with methanol. The title compound was obtained as an orange powder: 1.02 g, 98% yield. See Tables II and III for physical properties. Anal. Calcd for $(C_{20}H_{12}Si)_n$: C, 85.74; H, 4.82; Si, 10.00. Found: C, 81.92; H, 4.87; Si, 9.30; O, 0.27.

**Poly[(phenylsilylene)diacetylene] (10).** The general procedure was used with 1,4-bis(bromomagnesio)-1,3-butadiyne and gave 1.34 g (87% yield) of the title compound as a powder. Treatment with methanol to substitute the Si–Cl terminations was performed at −30 °C. See Tables II and III for physical properties. Anal. Calcd for $(C_{10}H_6Si)_n$: C, 77.92; H, 3.89; Si, 18.18. Found: C, 74.85; H, 3.98; Si, 18.60; O, 2.05.

**Poly[(bis(trimethylsilyl)silylene)diacetylene] (11).** The general procedure was used and gave 1.85 g (85% yield) of the title compound as an orange powder. See Tables II and III for physical properties. Anal. Calcd for $(C_{10}H_{18}Si_3)_n$: C, 54.05; H, 8.11; Si, 37.84. Found: C, 52.87; H, 8.19; Si, 35.00; O, 4.10.

**Poly[(diphenylgermylene)diacetylene] (12).** The following procedure is given as an example for the synthesis of the poly[(germylene)diacetylenes].

Dibromodiphenylgermane (0.012 mol, 2.6 mL) was added neat, via a syringe, to a slurry of the dilithio reagent (0.01 mol) in THF (50 mL), the medium being maintained at room temperature. The reaction mixture turned yellow and became limpid; it was stirred for 12 h. A solution of MeMgBr (0.003 mol) was added to substitute the Ge–Br bonds of the ends of the chains, and the mixture was stirred for 1 h. The medium was hydrolyzed using a saturated solution of $NH_4Cl$ and extracted with $CH_2Cl_2$. The organic phase was dried over $MgSO_4$ and concentrated under vacuum. Addition of pentane gave a beige powder of the title compound: 2.4 g, 87% yield. See Tables II and IV for physical properties. UV (THF; $\lambda_{max}$, nm): 244, 260, 273. Anal. Calcd for $(C_{16}H_{10}Ge)_n$: C, 69.91; H, 3.64; Ge, 26.43. Found: C, 68.2; H, 3.7; Ge, 27.6; O, 0.7.

**Poly[(methylphenylgermylene)diacetylene] (13).** The same procedure as for 12 was used, with 0.012 mol (3.9 g) of methylphenyldibromogermane and 0.01 mol of the dilithio reagent. After hydrolysis, the medium was extracted twice with $Et_2O$ (instead of $CH_2Cl_2$) and after standard workup gave an oil which was dried under vacuum to give a beige powder of the title compound: 1.65 g, 79% yield. See Tables II and IV for physical properties. UV (THF; $\lambda_{max}$, nm): 244, 260, 274. Anal. Calcd for $(C_{11}H_8Ge)_n$: C, 62.08; H, 3.76; Ge, 34.15. Found: C, 60.88; H, 3.97; Ge, 31.15; O, 0.7.

**Poly[(ethylphenylgermylene)diacetylene] (14).** The same procedure as for 12 was used, with 0.012 mol (3.49 g) of ethylphenyldibromogermane and 0.01 mol of the dilithio reagent. After hydrolysis, the medium was extracted twice with $Et_2O$ (instead of $CH_2Cl_2$). A beige powder (1.65 g) was obtained in 65% yield. See Tables II and IV for physical properties. UV (THF; $\lambda_{max}$, nm): 244, 257, 274. Anal. Calcd for $(C_{12}H_{10}Ge)_n$: C, 63.5; H, 4.4; Ge, 34.15. Found: C, 61.37; H, 4.59; Ge, 32.3; O, 1.9.

**Poly[(diethylgermylene)diacetylene] (15).** The same procedure as for 12 was used, with 0.012 mol (1.85 mL) of diethyldibromogermane and 0.01 mol of the dilithio reagent. A white powder of the title compound was obtained: 0.9 g, 50% yield. See Tables II and IV for physical properties. UV (THF; $\lambda_{max}$, nm): 243, 256, 273. Anal. Calcd for $(C_8H_{10}Ge)_n$: C, 53.75; H, 5.6; Ge, 40.65. Found: C, 50.44; H, 6.38; Ge, 40.7; O, 0.12.

**Conductivity Measurements.**[23] A solution of $FeCl_3$ (0.1 M) in $CH_2Cl_2$ was added to a solution of the polymer dissolved in $CH_2Cl_2$ in order to have a $[FeCl_3]/[polymer]$ ratio between 0.3 and 0.5, which corresponds to one doping anion per two or three acetylene units. The doped polymer has been cast into a thin film on a glass substrate by slow evaporation of the solvent. The thickness of the film (typically 20–200 μm) was determined using a Sylvac Model 25 instrument. The conductivity was measured using the four-probe method with gold electrodes.[21] See Table V for conductivity values.

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**Registry No.** **1** (copolymer), 128359-07-9; **1** (SRU), 128599-08-6; **2** (copolymer), 140391-12-4; **2** (SRU), 140391-19-1; **3** (copolymer), 128359-15-9; **3** (SRU), 128599-15-5; **4** (copolymer), 128359-08-0; **4** (SRU), 128599-09-7; **5** (copolymer), 128359-14-8; **5** (SRU), 31693-69-3; **6** (copolymer), 128359-10-4; **6** (SRU), 128599-11-1; **7** (copolymer), 128359-12-6; **7** (SRU), 128599-13-3; **8** (copolymer), 128359-09-1; **8** (SRU), 128599-10-0; **9** (copolymer), 140391-13-5; **9** (SRU), 140409-96-7; **10** (copolymer), 140391-14-6; **10** (SRU), 140391-20-4; **11** (copolymer), 140409-95-6; **11** (SRU), 140409-97-8; **12** (copolymer), 140391-15-7; **12** (SRU), 31693-72-8; **13** (copolymer), 140391-16-8; **13** (SRU), 140391-21-5; **14** (copolymer), 140391-17-9; **14** (SRU), 140391-22-6; **15** (copolymer), 140391-18-0; **15** (SRU), 140391-23-7; $HMe_2Si(C{\equiv}C)_2SiMe_2H$, 31098-30-3; $PhMe_2Si(C{\equiv}C)_2SiMe_2Ph$, 140391-04-4; $Ph_2MeSi(C{\equiv}C)_2SiMe_2Ph$, 140391-05-5; $Ph_3Si(C{\equiv}C)_2SiPh_3$, 140391-06-6; $HPh_2Si(C{\equiv}C)_2SiPh_2H$, 140391-07-7; $(MeO)_3Si(C{\equiv}C)_2Si(OMe)_3$, 140391-08-8; $(EtO)_3Si(C{\equiv}C)_2Si(OEt)_3$, 140391-09-9; $Et_3Ge(C{\equiv}C)_2GeEt_3$, 96326-00-0; $PhMe_2Ge(C{\equiv}C)_2GeMe_2Ph$, 140391-10-2; $MePh_2Ge(C{\equiv}C)_2GePh_2Me$, 140391-11-3; $Ph_3Sn(C{\equiv}C)_2SnPh_3$, 1262-93-7; $Li(C{\equiv}C)_2Li$, 65864-08-6; $ClMe_2SiPh$, 768-33-2; $ClPh_2SiMe$, 144-79-6; $ClPh_3Si$, 76-86-8; $ClMe_2SiH$, 1066-35-9; $ClPh_2SiH$, 1631-83-0; $Cl(MeO)_3Si$, 4668-00-2; $Cl(EtO)_3Si$, 4667-99-6; $BrEt_3Ge$, 1067-10-3; $BrMe_2PhGe$, 134695-21-9; $BrMePh_2Ge$, 27663-93-0; $Ph_3SnCl$, 639-58-7; $Li(C{\equiv}C)_2TMS$, 73084-25-0; $BrPh_3Sn$, 962-89-0; $FeCl_3$, 7705-08-0.

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