significantly affect the charge-transport characteristics. Variable-temperature four-probe electrical conductivity and thermoelectric power data for the present fibers are shown in parts A and B of Figures 2, respectively. These charge-transport data are remarkably similar to data for high-quality samples of chemically prepared or electropolymerized polypyrrole. In particular, the conductivity data can be best fit to a variable-range hopping model (eq 1),[10,16,20,21] while the thermoelectric power is metallic and

$$\sigma = \sigma_0 e^{-(T_0/T)^{1/4}} \quad (1)$$

p-type (S~T).[10,16,20,21] These results suggest a continuous polypyrrole conducting network extending along the fiber axis.

In summary, the present results demonstrate that ultrahigh-modulus polymer–conductive polymer alloys can be straightforwardly prepared by using N-metalated PPTA (Kevlar) in organic solvents. It is evident that this approach should be amenable both to other polymer–PPTA hybrid materials and to large-scale processing. Further exploration of these directions as well as studies of fiber processing/microstructure/charge transport/mechanical properties correlations are in progress.

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Organosilicon Polymers: Synthesis of Poly[(silanylene)diethynylene]s with Conducting Properties[1]

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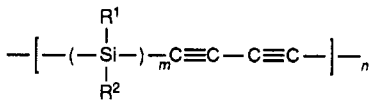
In recent years, much attention has been focused on the synthesis of one-dimensional organometallic polymers as a source of novel materials in terms of their optical and electronic properties or as precursors for ceramics.[2]

In this context, we are investigating polyyne polymers, **1**, in which the alternate arrangement of a silanylene unit



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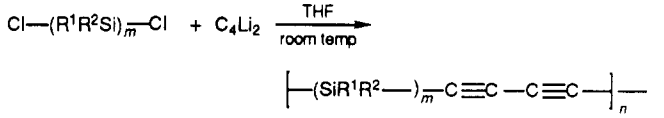
and a diyne group is found regularly in the polymer backbone. These polymers are of interest in terms of the possible effects of dπ(Si atoms)–pπ(acetylenic carbons) conjugation on their properties.[3] Such molecules might be expected to exhibit properties consistent with the delocalization of the π-electron density along the main chain.[4]

Previous attempts to prepare such polymers either by copper-catalyzed oxidative coupling reaction[5] or by thermal polymerization of $R_2Si(C{\equiv}CH)_2$[6,7] have failed to produce

Table I. Characteristics of the Poly[(silanylene)diethynylene]s[a] 1:



dichlorosilane	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$	n_w	mp, °C	conductivity,[d] S/cm^{-1}
Me_2SiCl_2	4063	1.24	38	150	8×10^{-5}
$MePhSiCl_2$[e]	3068	1.64	18	80–110	10^{-4}
$Me(CH_2{=}CH)SiCl_2$[b]	2154	1.51	18	oil	
$Me(p\text{-}MeC_6H_4)SiCl_2$[e]	2712	1.30	15	90–130	2×10^{-4}
$Me(p\text{-}FC_6H_4)SiCl_2$[e]	1790	1.31	10	oil	
$Me(p\text{-}MeOC_6H_4)SiCl_2$[e]	1822	1.24	9	90–120	3×10^{-4}
$Me(p\text{-}CF_3C_6H_4)SiCl_2$[e]	1612	1.25	7	oil	
Ph_2SiCl_2	1826	1.31	8	80–120	3×10^{-3}
$(Me_2ClSi)_2$[b,f]	3536	1.41	21	100–140	5×10^{-5}

[a] Experimental conditions: reactions are carried out in THF at room temperature for 12 h. [b] The di-Grignard reagent[8] has been used instead of C_4Li_2. [c] Molecular weights have been determined by using GPC and relative to polystyrene standards (solvent THF). [d] Upon doping with 0.3–0.5 mol of $FeCl_3$ in solution (0.1 M in CH_2Cl_2) per mol of C≡C units. [e] $MeArSiCl_2$ are prepared by reaction of the respective Grignard reagent (ArMgX) with a large excess of $MeSiCl_3$ using conventional methods. [f] $(Me_2ClSi)_2$ is obtained from hexamethyldisilane according to the method described in ref 14.

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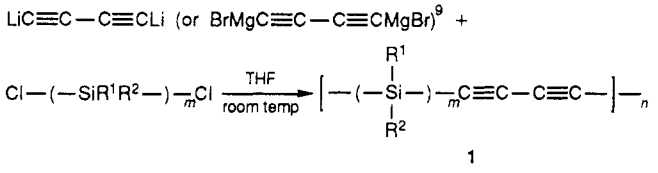
the expected compounds. Very recently, Ishikawa et al.[8] described described synthesis of two poly[(disilanylene)-diethynylene]s. This has prompted us to report the preliminary results of our concurrent studies.[1] We have found that the reaction of a dichlorosilane, $Cl(SiR^1R^2)_mCl$, and the dilithium or di-Grignard reagents of the diacetylene results in the formation of a polymer of the form 1:



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(m = 1 or 2, R^1 or R^2 = alkyl, aryl, or vinyl; n is indicated in Table I). Thus, when a dilute (0.25 M) solution of the dilithiobutadiyne, preferentially prepared from the 1,4-bis(trimethylsilyl)-1,3-butadiyne (25 mmol) via a double desilylation with the MeLi–LiBr complex (50 mmol) in THF[10-12] was treated with a slight excess of neat Me_2SiCl_2 (27 mmol) at room temperature for 12 h, a cream-colored glassy solid was obtained after quenching the reaction mixture with MeOH and removal of the solvents. The resulting substance was recrystallized from hexane to yield 2.50 g of solid.[13] The polymer thus obtained is soluble in organic solvents such as THF, dichloromethane, and toluene and it melts at 150 °C with decomposition. The molecular weight ($\bar{M}_w$) of 1 (R^1 = R^2 = Me, m = 1) was determined by using GPC and found to be 4063 relative to polystyrene standards ($\bar{M}_w/\bar{M}_n$ = 1.24). The presence of the [(silanylene)diethynylene] unit in the polymer backbone was clearly confirmed by its IR spectrum [ν(C≡C) 2070 cm^{-1}] and ^{13}C NMR spectrum [−0.1 (Me_3Si), 82.3, and 89.3 ppm (acetylenic carbons)].

In this manner, a variety of new polymers of the type 1 have been produced in good yields, as summarized in Table I.

The reaction took place readily under mild conditions. Moreover various side groups, such as aromatic rings with either electron-donating (Me, MeO, and F) or -withdrawing substituents (CF_3), and a disilanylene unit (m = 2) have been introduced. In the case of the vinylmethyldichlorosilane as a starting material, the di-Grignard reagent[9] was used instead of C_4Li_2 to avoid the addition of the dilithio derivative across the double bond[15] and, thus, cross-linking reactions. Finally, we wish to point out the particular thermal stability of polymers 1 (as contrasted with the usual polyynes[16]). No degradation reaction occurred below 150 °C.

Polymers 1 can be cast into thin films by spin coating from their CH_2Cl_2 solution, leading to insulating films. The doping of these polymers has been carried out by the use of an electron acceptor in CH_2Cl_2 solution, previously deoxygenated by argon bubbling. The required amount of the dopant, $FeCl_3$ (0.1 M in CH_2Cl_2), is added to the polymer solution. The mixture is stirred until the characterisitic dark color of the doped state of the polymer appears. Films of doped polymers are then formed from these solutions by spin coating on a glass substrate. The thickness of these films is measured with a Sylvac 25 thickness monitor. Electrical conductivities are measured by the four-point method.[17]

In the undoped state, these organosilicon polymers are insulators with conductivity values ranging from 10^{-12} to 10^{-15} S cm^{-1}. When they are doped with the acceptor $FeCl_3$, their conductivity increases dramatically, reaching the range 10^{-3}–10^{-5} S cm^{-1} (Table I). These relatively high conductivity values are comparable to those obtained with fully conjugated organic polymers, such as poly(*N*-methylpyrrole).[18] They show that a Si atom inserted into a conjugated polymeric carbon backbone still allows charge delocalization. The results also show that the presence of two consecutive Si atoms in the chain (last entry, Table I) does not prevent conductivity in the polymer. We have also observed that the use of a stronger acceptor, such as HNO_3 or SbF_5, leads to higher conductivity values, as recently confirmed by Ishikawa et al. in the poly[(disilanylene)diethynylene] series.[8,19] However, the doped state obtained with these latter acceptors is not stable enough to ensure long-term reproducibility. Furthermore, an important conclusion drawn from Table I concerns the possibility of modulating the charge-transport properties by electronic effects of substituents grafted on the Si atom. Thus electron-donating substituents significally enhance the conductivity value by increasing the electron density on the Si atom. These conclusions agree with the reported results on organosilicon polymers.[20] Taking into account the ease of functionalization provided by the silicon atom and the particular stability of this class of polymers, the poly[(silanylene)diethynylene]s appear very promising for the design of new functionalized electrically conducting polymers.

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