**Figure 3.** Gel permeation chromatograms of dendrimers 1, 2, and 1,3,5-triphenylbenzene.

(Figure 2).[16] Gel permeation chromatography of 1–4 resulted in a single peak for each with polydispersity below the resolution limit of the technique (Figure 3). The UV spectra of 1 and 2 showed broad maxima centered at 260 nm with extinction coefficients of $1.41 \times 10^5$ and $3.63 \times 10^5$ M$^{-1}$ cm$^{-1}$. The UV spectra and the absence of color in 1 and 2 indicate that 1,3,5-triphenylbenzene is a good model for the chromophore in 1 and 2.

Mass spectra of the dendrimers 1, 2, and 4 (fast atom bombardment) show clean parent ions for each compound. The dendrimers 1–4 are thermally stable (>350 °C in air) and, unlike dendrimers based upon alkyl amides, do not discolor or aggregate upon standing in solution.[17] This stability may be an important factor in developing applications for these materials as for , e.g., X-ray beam calibration standards. We are actively pursuing our investigations of these materials and other larger aromatic dendrimers in which phenyl rings are separated by amide, ester, and acetylenic units. Results of these approaches will be the subject of future reports.

**Acknowledgment.** We acknowledge helpful discussions with E. A. Chandross and thank Elizabeth W. Kwock for gel permeation chromatographic data.

(16) This supports the notion of a branch cell hierarchy as described in ref 2.

(17) Starburst dendrimers based upon poly(alkylamides) have recently become commercially available from Polysciences, Warrington, PA, under license from The Dow Chemical Co. The accompanying literature recommends storing the materials under an atmosphere of nitrogen, at 4 °C, and at pH close to 7. Deviations from these conditions are reported to lead to discoloration and aggregation of materials.

# Electrically Conductive Polymer–Ultra-High-Modulus Polymer Alloys. A Solution Processing Route to Hybrid Fibers of Kevlar–Polypyrrole

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An attractive approach to enhancing the mechanical properties, environmental stability, processability, and other desirable characteristics of electrically conductive polymers[1] is to prepare hybrid materials in which they are

**Table I. Properties of PPTA–Polypyrrole Fibers**

| spin-draw ratio | diameter, μm | polypyrrole content,[a] wt % | $\sigma$(300 K), S/cm |
|---|---|---|---|
| 1.0[b] | 220 | 59.2 | 7.7 |
| 1.3 | 74 | 57.2 | 0.6 |

[a] From elemental analysis. See footnote 17 for data. [b] A takeup drum was not employed.

"alloyed" with polymers having complementary properties.[2] In the case of polypyrrole,[1,3] composite films have been prepared electrochemically on a small scale with poly(vinyl alcohol),[4] poly(vinyl chloride),[5] polyurethane,[6] and polystyrene.[7] Although such materials have useful characteristics, it would also be of great interest to prepare polypyrrole alloys with fiber-forming ultrahigh-modulus polymers such as poly(p-phenyleneterephthalamide) (PPTA, Kevlar).[8] However, the intractability of conventional polypyrrole,[3,9] and the traditional approach of processing of PPTA from strong acids[8,10] present a serious obstacle. In this communication, we report a successful route to PPTA–polypyrrole hybrid fibers[11] that capitalizes upon the high solubility of N-metalated PPTA[12] and pyrrole in polar organic solvents.

In a typical preparation, distilled pyrrole (50–80 wt % of the final solution) was added to a dry DMSO solution of N-NaPPTA,[13] and the resulting red solution was stirred at room temperature under inert atmosphere. It was noted that the viscosity of the solution decreases markedly upon addition of pyrrole. This may arise from N-NaPPTA carbonyl group–pyrrole hydrogen bonding and/or partial

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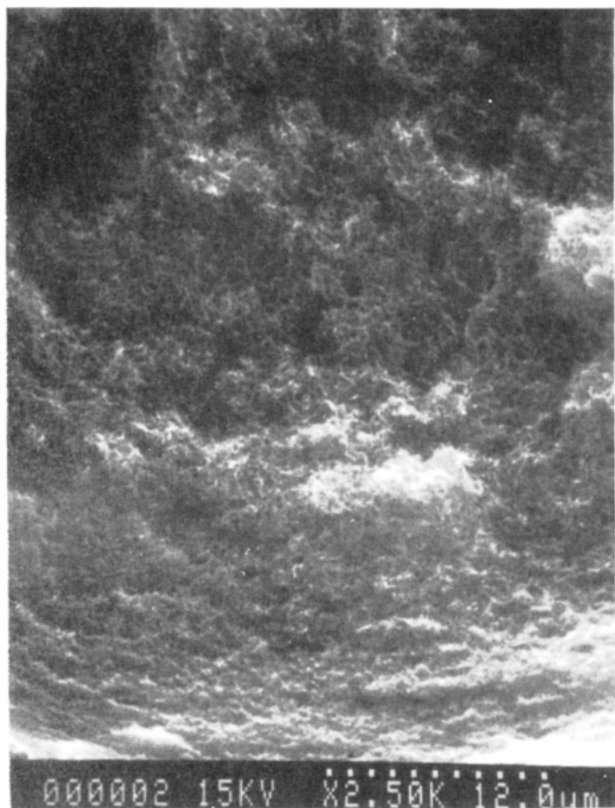
**Figure 1**. Scanning electron micrograph of a PPTA/polypyrrole fiber viewed in cross section. Spin-draw ratio = 1.0.

transmetalation.[14] With the processing apparatus described previously,[2b,10a,b,d] the *N*-NaPPTA/pyrrole solution was dry-jet wet-spun (with or without a takeup drum) into an aqueous ferric chloride coagulation bath (30–40 wt % $FeCl_3 \cdot 6H_2O$). The coagulation process effects rapid oxidative polymerization of the pyrrole[1,3,9] and protonic regeneration[15] of PPTA. After repeated washing with water and acetone, followed by drying under vacuum at room temperature, the resulting black fibers are qualitatively strong and flexible.

The composition and microstructure of representative PPTA/polypyrrole fibers were investigated by elemental analysis and scanning electron microscopy (SEM). The former data indicate that the materials are greater than 50% polypyrrole by weight (Table I) and that the stoichiometry of the polypyrrole component is not unusual for an $FeCl_3$-induced pyrrole polymerization.[3,10,16,17] Anions resulting from such a process have been variously reported to be $Cl^-$, $FeCl_4^-$, and $FeCl_6^{-3}$.[16] SEM photographs of fiber cross sections indicate a microstructure consisting of microfibrils having ca. 100-nm diameter extending in the extrusion direction (Figure 1). The packing of the fibrils is denser in the fibers spun with a higher draw ratio.
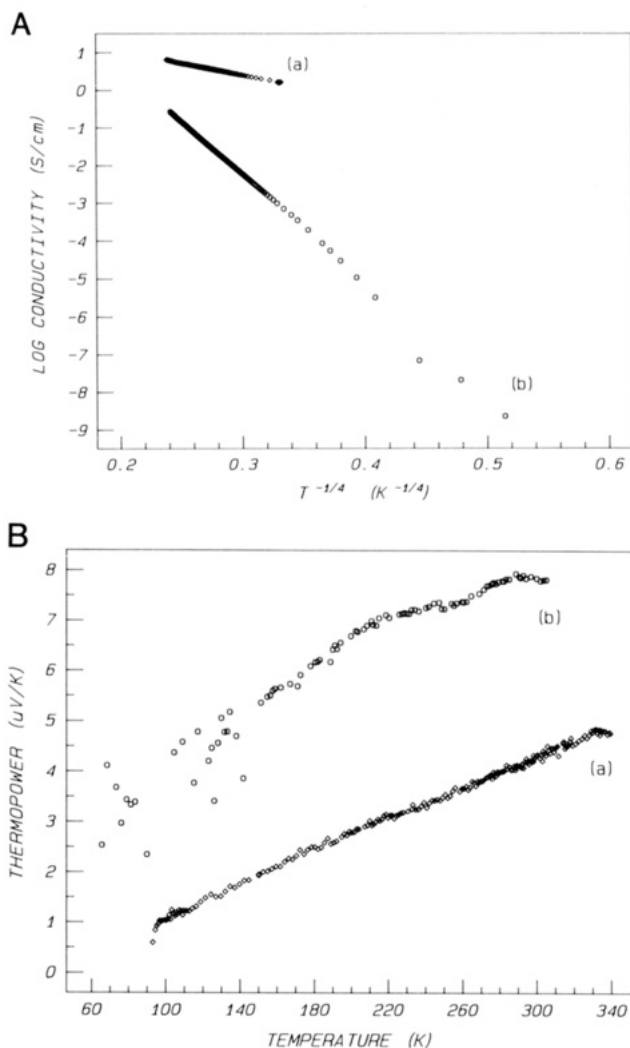


**Figure 2**. (A) Variable-temperature four-probe electrical conductivity data for two PPTA/polypyrrole fibers spun at the spin-draw ratios (a) 1.0 and (b) 1.3. (B) Variable-temperature thermoelectric power data for two PPTA/polypyrrole fibers spun at the spin-draw ratios (a) 1.0 and (b) 1.3. The low-temperature scatter in the data for the latter fiber is due to the high resistivity at these temperatures.

Scanning EDAX maps of fiber cross sections indicate a slightly higher ($\sim 10\%$) chlorine content in the outer regions of the fibers. This is consistent with some diffusion of pyrrole toward the exterior of the fiber during coagulation process and subsequent exposure to the $FeCl_3$ solution. In agreement with these results, an iron map of the spin-draw ratio = 1.3 fiber shows iron to be located primarily in the outer regions of the fiber.[18]

Variable-temperature four-probe electrical conductiivty and thermoelectric power measurements were carried out using the instrumentation and methods described previously.[10b,d,19] Fiber and contact dimensions were measured with a metallurgical microscope. The maximum room-temperature conductivity of a PPTA/polypyrrole fiber is $\sim 8$ S/cm, which is considerably higher than that of a neat polypyrrole sample prepared by an identical $FeCl_3$ oxidative procedure (0.2 S/cm as a pressed pellet). Removing the outer layer of the fiber with a razor blade does not

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(17) Anal. Calcd for $(PPTA)_{0.18}[(C_4H_3NO_{0.15})Fe_{0.009}Cl_{0.28}]_{0.82}$ (spin-draw ratio = 1.0): C, 64.7; H, 4.0; N, 15.3; O, 7.3; Fe, 0.39; Cl, 7.6. Found: C, 64.7; H, 4.7; N, 15.3; O, 7.3 (by difference); Fe, 0.39; Cl, 7.6. Calcd for $(PPTA)_{0.21}[(C_4H_3NO_{0.77})Fe_{0.034}Cl_{0.13}]_{0.79}$ (spin-draw ratio = 1.3): C, 62.7; H, 4.0; N, 14.5; O, 14.1; Fe, 1.3; Cl, 3.1. Found: C, 62.6; H, 4.3; N, 14.5; O, 14.1 (by difference); Fe, 1.3; Cl, 3.1. No Na was detected in either fiber by EDAX. Polypyrrole films commonly exhibit high hydrogen and oxygen contents.[1,3,16]

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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

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

p-type $(S \sim T)$.[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

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

Cl—$(R^1R^2Si)_{\overline{m}}$—Cl + C$_4$Li$_2$ $\xrightarrow[\text{room temp}]{\text{THF}}$

$\left[\!\!\left[-(SiR^1R^2\!-\!)_{\overline{m}}\!-C\!\equiv\!C\!-\!C\!\equiv\!C\!-\right]\!\!\right]\!\!\frac{}{n}$

| dichlorosilane | $\bar{M}_w{}^c$ | $\bar{M}_w/\bar{M}_n$ | $n_w$ | mp, °C | conductivity,[d] S/cm$^{-1}$ |
|---|---|---|---|---|---|
| Me$_2$SiCl$_2$ | 4063 | 1.24 | 38 | 150 | $8 \times 10^{-5}$ |
| MePhSiCl$_2{}^e$ | 3068 | 1.64 | 18 | 80–110 | $10^{-4}$ |
| Me(CH$_2$=CH)SiCl$_2{}^b$ | 2154 | 1.51 | 18 | oil | |
| Me($p$-MeC$_6$H$_4$)SiCl$_2{}^e$ | 2712 | 1.30 | 15 | 90–130 | $2 \times 10^{-4}$ |
| Me($p$-FC$_6$H$_4$)SiCl$_2{}^e$ | 1790 | 1.31 | 10 | oil | |
| Me($p$-MeOC$_6$H$_4$)SiCl$_2{}^e$ | 1822 | 1.24 | 9 | 90–120 | $3 \times 10^{-4}$ |
| Me($p$-CF$_3$C$_6$H$_4$)SiCl$_2{}^e$ | 1612 | 1.25 | 7 | oil | |
| Ph$_2$SiCl$_2$ | 1826 | 1.31 | 8 | 80–120 | $3 \times 10^{-3}$ |
| (Me$_2$ClSi)$_2{}^{b,f}$ | 3536 | 1.41 | 21 | 100–140 | $5 \times 10^{-5}$ |

[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$_4$Li$_2$. [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$_2$Cl$_2$) 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$_2$ClSi)$_2$ is obtained from hexamethyldisilane according to the method described in ref 14.

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

$$-\left[\!-(\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\mid\atop\mid}}\!\!Si\!-\!)_{\overline{m}}C\!\equiv\!C\!-\!C\!\equiv\!C\!-\right]\!-_n$$

**1**
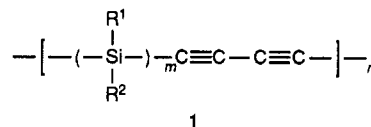
and a diyne group is found regularly in the polymer backbone. These polymers are of interest in terms of the possible effects of d$\pi$(Si atoms)–p$\pi$(acetylenic carbons) conjugation on their properties.[3] Such molecules might be expected to exhibit properties consistent with the delocalization of the $\pi$-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$_2$Si(C≡CH)$_2$[6,7] have failed to produce

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