# Spinning Fibres and Fibre Blends of an Electrically Conductive Polymer

**Tamotsu Inabe,[a] Joseph W. Lyding,[b] and Tobin J. Marks*[a]**

[a] *Department of Chemistry,* [b] *Department of Electrical Engineering and Computer Science, and the Materials Research Center,[a,b] Northwestern University, Evanston, Illinois 60201, U.S.A.*

Acid solutions of $[Si(Pc)O]_n$ (Pc = phthalocyaninato), with or without an added 'aramid' polymer can be wet-spun to yield, after halogen doping, air-stable fibres with thermally activated conductivities as high as 2 $\Omega^{-1}$ cm$^{-1}$.

Despite the recent progress in controlling the properties of electrically conductive macromolecular solids,[1] many of these substances exhibit significant limitations with respect to air, water, and thermal stability, microstructural control, mechanical stability, and, in particular, processability. We are concerned with some of these issues here, and report an approach to solution processing the robust, confacially joined metallomacrocyclic polymer $[Si(Pc)O]_n$ (Pc = phthalocyaninato)[2] either alone or, by virtue of similar solubility properties, as a blend with a high-modulus, orientable 'aramid' polymer such as 'Kevlar' (1).[3] The result, in optimum cases, is strong, flexible, preferentially oriented, electrically conductive fibres.

Concentrated solutions of $[Si(Pc)O]_n$ (7—30 weight %) can be prepared in trifluoromethanesulphonic acid. Extrusion of these solutions at 80 °C into an aqueous coagulation bath using an anaerobic, Teflon-lined version of the spinning apparatus described elsewhere,[4] results in air-stable, darkly coloured fibres. Iodine doping (partial oxidation[5]) can be achieved by introducing $I_2$ into the spinning solution, immersing the resulting fibres in an $I_2$–benzene solution, or adding KI plus $I_2$ to the precipitation bath. The mechanical properties (strength, flexibility) of these fibres, which are brittle, can be significantly improved by adding Kevlar, which is also acid-processable,[3] to the spinning solution (1—7 weight %). Iodine doping can then be carried out as above. Fibre stoicheiometries were established by elemental analysis. As assessed by appearance, mechanical properties, and electrical conductivity, the fibres appear to be stable in air for many months.

Electrical conductivity measurements were performed with the automated instrumentation described elsewhere,[2a] using standard 4-probe d.c. methodology. Blocking electrode measurements indicated that ion conduction was insignificant.
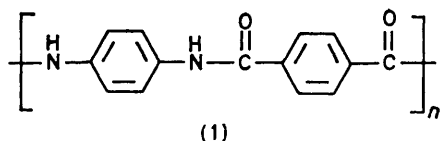
Conductivity data are set out in Table 1, and representative variable temperature plots, all of which reveal thermally activated charge transport, are shown in Figure 1. Significant conductivity increases compared with that of $[Si(Pc)O]_n$ are achieved even without $I_2$ doping. Based upon the sulphur content of these fibres (ca. 0.5%, presumably as $CF_3SO_3H$ or $CF_3SO_3^-$) and analogous observations for polyacetylene,[1b] we tentatively ascribe this result to 'acid doping.' It can also be seen (Figure 1A) that the $I_2$-doped fibre is more conductive than an $\{[Si(Pc)O]I_y\}_n$ compaction. In this case, the result is more likely to be due to diminished interparticle contact resistance than to preferential orientation of the $[Si(Pc)O]_n{}^{\delta+}$ chains (vide infra). The charge transport data also reveal an increase in room temperature conductivity with increasing $[Si(Pc)O]_n$ content of the $[Si(Pc)O]_n$–Kevlar–$I_2$ blends. Curiously, however, the phenomenological 'activation energies' derived from fitting ln $\sigma$ vs. $1/T$ plots are relatively insensitive to the increasing $[Si(Pc)O]_n$ content. This behaviour may reflect the inhomogeneous structural nature of the blends (vide infra) in which $[Si(Pc)O]_n{}^{\delta+}$-mediated conduction pathways increase in cross-sectional area with increasing $[Si(Pc)O]_n$ content, while interparticle contacts giving rise to activated behaviour remain
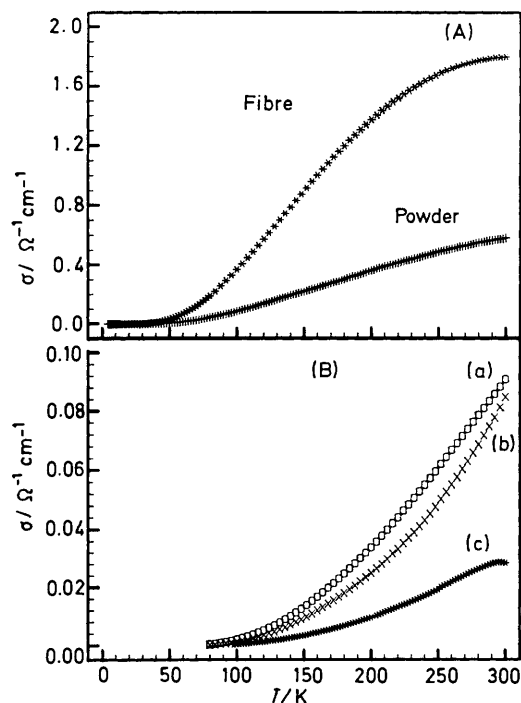


(1)

**Table 1.** Four-probe electrical conductivity data for $[Si(Pc)O]_n$–Kevlar fibres.

| Composition[a] | Conductivity ($\sigma$) at 300 K $\Omega^{-1}$ cm$^{-1}$ | Activation energy[b] ($\Delta$)/eV |
|---|---|---|
| $\{[Si(Pc)O]I_{1.76}\}_n$[c] | 1.8 | $2.10 \times 10^{-2}$ |
| $\{[Si(Pc)O](Kev.)_{0.59}I_{1.45}\}_n$[d] | $9.1 \times 10^{-2}$ | $4.79 \times 10^{-2}$ |
| $\{[Si(Pc)O](Kev.)_{0.98}I_{1.57}\}_n$[c] | $8.5 \times 10^{-2}$ | $5.13 \times 10^{-2}$ |
| $\{[Si(Pc)O](Kev.)_{4.38}I_{3.69}\}_n$[d] | $2.9 \times 10^{-2}$ | $5.27 \times 10^{-2}$ |
| $\{[Si(Pc)O](Kev.)_{0.73}\}_n$ | $2.5 \times 10^{-3}$ | $12.0 \times 10^{-2}$ |
| $[Si(Pc)O]_n$[e] | $5.5 \times 10^{-6}$ | $29 \times 10^{-2}$ |

[a] Pc = Phthalocyaninato; Kev. = Kevlar monomer unit (1); all samples contain traces of sulphur. [b] Obtained via a least-squares fit of the equation $\sigma = A \exp(-\Delta/kT)$. [c] Doping with $C_6H_6$–$I_2$. [d] Doping with aqueous KI–$I_2$. [e] Compaction measurement from ref. 2a.



**Figure 1.** (A) Variable-temperature four-probe electrical conductivity data for an $\{[Si(Pc)O]I_{1.76}\}$ fibre and a polycrystalline compaction of approximately the same stoicheiometry. (B) Variable-temperature four-probe electrical conductivity data for $[Si(Pc)O]_n$–Kevlar fibres of composition: (a) $\{[Si(Pc)O](Kev)_{0.59}I_{1.45}\}_n$; (b) $\{[Si(Pc)O](Kev)_{0.98}I_{1.57}\}_n$; (c) $\{[Si(Pc)O](Kev.)_{4.38}I_{3.69}\}_n$. Kev. = Kevlar monomer unit (1).

essentially constant. This observation and a satisfactory fit of the conductivity data to equation (1)[6] suggest a transport mechanism involving thermal fluctuation-induced tunnelling between conductive domains in an inhomogeneous medium.[2a,6] Control experiments indicate that pure Kevlar fibres spun by the same procedure absorb minimal halogen and are electrical insulators.

$$\sigma = \sigma_0 \exp[-T_1/(T + T_0)] \qquad (1)$$

With regard to microstructure (and possible phase separation), preliminary wide angle $X$-ray diffraction studies of the fibres by photographic (Laue) and diffractometric techniques[7] reveal minimal detectable preferential chain orientation in the $[Si(Pc)O]_n-I_2$ fibres. However, the diffraction data on the $[Si(Pc)O]_n-Kevlar-I_2$ fibres reveal superimposed patterns of $\{[Si(Pc)O]I_{1\cdot1}\}_n$[2a] and Kevlar,[3] with preferential orientation[7]† of the respective chain axes in the longitudinal fibre direction. Kevlar contents as low as 3 weight % give rise to detectable preferential orientation[7]† of the $\{[Si(Pc)O]I_{1\cdot1}\}_n$ crystalline domains. Resonance Raman spectra[8a] reveal the presence of $I_3^-$ as the predominant polyiodide, consistent with oxidation of the metallomacrocyclic arrays and the $\{[Si(Pc)O]I_{1\cdot1}\}_n$ crystal structure.[2a] High resolution solid-state cross-polarisation magic-angle-spinning $^{13}C$ n.m.r. spectra of the blends reveal superimposed patterns of Kevlar and partially oxidized $[Si(Pc)O]_n^{\delta+}$ chains.[8b]

Beyond the rather specific example of $[Si(Pc)O]_n-Kevlar$ cited here, the present approach to constructing electroactive, oriented organic solids from conductive organic components and structure-reinforcing macromolecular hosts with similar solubility properties may have significant generality.

† A more quantitative analysis is in progress.

## References

1 (a) K. J. Wynne and G. B. Street, *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**, 23; (b) S. Etemad, A. J. Heeger, and A. G. MacDiarmid, *Annu. Rev. Phys. Chem.*, 1982, **33**, 443; (c) R. H. Baughamn, J. L. Brédas, R. R. Chance, R. L. Elsenbaumer, and L. W. Shacklette, *Chem. Rev.*, 1982, **82**, 209; G. Wegner, *Angew. Chem., Int. Ed. Eng.*, 1981, **20**, 361.
2 (a) B. N. Diel, T. Inabe, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, 1983, **105**, 1551; (b) C. W. Dirk, T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *ibid.*, 1983, **105**, 1539; T. Inabe, J. W. Lyding, M. K. Moguel, C. R. Kannewurf, and T. J. Marks, *Mol. Cryst. Liq. Cryst.*, 1983, **93**, 355; C. W. Dirk, K. F. Schoch, Jr., and T. J. Marks, in 'Conductive Polymers,' ed. R. D. Seymour, Polymer Science and Technology Series, vol. 15, Plenum Press, New York, 1981, pp. 209–226.
3 J. R. Schaefgen, T. Bair, J. W. Balou, S. L. K. Kwolek, P. W. Morgan, M. Panar, and J. Zimmerman in 'Ultra-high Modulus Polymers,' eds. A. Cifferi and I. M. Ward, Applied Science Publishers, London, 1979, pp. 173—201; G. B. Carter and V. T. J. Schenk in 'Structure and Properties of Oriented Polymers,' ed. I. M. Ward, Wiley, New York, 1976. ch. 13.
4 P. D. Sybert, W. H. Beever, and J. K. Stille, *Macromolecules*, 1981, **14**, 493.
5 T. J. Marks and D. W. Kalina in 'Extended Linear Chain Compounds,' ed. J. S. Miller, vol. 1, Plenum Press, New York, 1982, pp. 197—331.
6 J.-W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, *J. Chem. Phys.*, 1980, **73**, 946; P. Sheng, *Phys. Rev. B.*, 1980, **21**, 2180.
7 J. E. Pruiell and E. S. Clark, *Methods Exper. Phys.*, 1980, **16B**, 39; H. Tadokoro, 'Structure of Crystalline Polymers,' Wiley-Interscience, New York, 1979, ch. 4.
8 (a) J. F. Lomax and T. J. Marks, unpublished results; (b) P. J. Toscano and T. J. Marks, unpublished results.