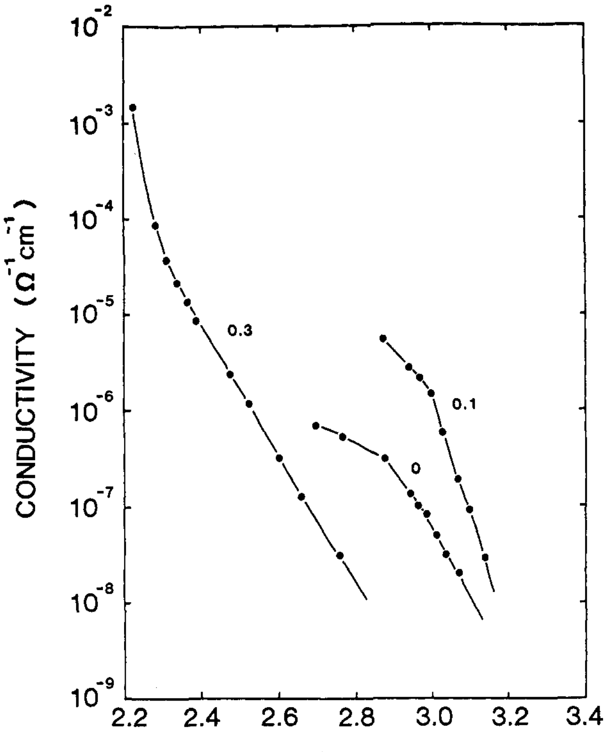

Figure 3. Conductivity as a function of reciprocal temperature for linear poly(ethylene imine) containing the molar ratios of NaI to monomer indicated on the curves. All data were obtained upon increasing the temperature.

dissolved, uncomplexed NaI crystals [indicated by asterisks in Figure 2] are first seen at a molar ratio of 0.3 and increase in intensity as the salt concentration is increased beyond that point. In other words, NaI in excess of 0.3 mol/mol of (CH_2CH_2NH) does not dissolve in or complex with the polymer but remains as a separate phase.

The dc conductivity as deduced from complex impedance measurements is shown as a function of reciprocal temperature in Figure 3. Data are for PEI containing 0.1 and 0.3 mol of NaI per mole of monomer repeat unit. We presume that the conductivity exhibited by the polymer to which we have not purposely added salt is due to ionic impurities, most likely sodium hydroxide left from the hydrolysis step in the synthesis of the polymer. The change in slope of conductivity vs. T^{-1} occurs when the semicrystalline polymer melts near 75 °C for the pure polymer and near 60 °C in the presence of 0.1 mol of NaI per mole of monomer. No evidence for a phase change below 150 °C is seen for the sample containing 0.3 mol of NaI per mole of polymer. Upon addition of 0.1 mol of NaI per mole of monomer repeat, the conductivity in the polymer at 60 °C increases from 6×10^{-8} (Ω cm)$^{-1}$ to 1.5×10^{-6} (Ω cm)$^{-1}$. However, when the molar ratio of NaI to polymer is increased to 0.3, conductivity is greatly reduced below values obtained before the purposeful addition of salt. Only at temperatures above 120 °C does the conductivity of the polymer containing 0.3 mol of NaI per mole of monomer exceed that of the starting polymer. The maximum in conductivity as a function of salt concentration has been observed in other polymer–salt systems[3,57] but the "pure" polymer has the lowest conductivity in those systems. As mentioned above, we have no assurance that all of the NaOH from the hydrolysis step has been removed from our sample. Steps were taken to remove the solvent used in preparing the films and precautions were taken to exclude moisture in subsequent steps as stated previously.

Linear poly(ethylene imine) has been shown to dissolve sodium iodide up to a maximum concentration of about 0.3 mol of NaI per mol of monomer repeat unit. At low concentrations, the salt interferes with the ability of the polymer to crystallize while at higher concentrations, the salt and polymer form a complex crystalline phase which melts near 150 °C. After melting the complex crystalline phase which formed upon evaporation of a mutual solvent for polymer and salt, it does not re-form upon cooling at the rates studied. The conductivity of the poly(ethylene imine) containing 0.1 mol ratio sodium iodide is 5×10^{-6} (Ω cm)$^{-1}$ at 75 °C, which is lower than the values commonly obtained for salt-containing poly(ethylene oxide). The demonstrated capability of nitrogen-containing polymers to dissolve salts as well as oxygen-containing polymers may help in the understanding of solid polymeric electrolytes with enhanced ionic conductivity near room temperature.

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References and Notes

(1) Fenton, D. E.; Parker, J. M; Wright, P. V. *Polymer* **1973**, *14*, 589.
(2) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. "Fast Ion Transport in Solids"; Vashishta, P., Mundy, J. N., Shenoy, G. K., Eds.; Elsevier North-Holland: New York, 1979; p 131.
(3) Chiang, C. K.; Davis, G. T.; Harding, C. A.; Aarons, J. *Solid State Ionics* **1983**, *9*, *10*, 1121.
(4) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91.
(5) Watanabe, M.; Nagaoka, K.; Kanba, M.; Shinohara, I. *Polym. J.* **1982**, *14*, 877.
(6) Watanabe, M.; Ikeda, J.; Shinohara, I. *Polym. J.* **1983**, *15*, 175.
(7) Watanabe, M.; Ikeda, J.; Shinohara, I. *Polym. J.* **1983**, *15*, 65.
(8) Shriver, D. F.; Papke, B. L.; Ratner, M. A.; Dupon, R.; Wong, T.; Brodwin, M. *Solid State Ionics* **1981**, *5*, 83.
(9) Dupon, R.; Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* **1984**, *131*, 586.
(10) Stainer, M.; Hardy, L. C.; Whitmore, D. H.; Shriver, D. F. *J. Electrochem. Soc.* **1984**, *131*, 784.
(11) Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules* **1972**, *5*, 108.
(12) Saegusa, T.; Ikeda, H.; Fujii, H. *Polym. J.* **1972**, *3*, 35.
(13) Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards nor does it imply that the materials or equipment identified is necessarily the best available for the purpose.
(14) Chiang, C. K.; Bethin, J. R.; Dragoo, A. L.; Franklin, A. D.; Young, K. F. *J. Electrochem. Soc.* **1982**, *129*, 2113.
(15) Chatani, Y.; Tadokoro, H.; Saegusa, T.; Ikeda, H. *Macromolecules* **1981**, *14*, 315.
(16) Chatani, Y.; Kobatake, T.; Tadokoro, H.; Tanaka, R. *Macromolecules* **1982**, *15*, 170.
(17) Chatani, Y.; Kobatake, T.; Tadokoro, H. *Macromolecules* **1983**, *16*, 199.

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New Route to Carbon Fibers: Pyrolysis of Poly(cyanogen)

In a recent paper,[1] we have described the electropolymerization of cyanogen (ethanedinitrile) in acetonitrile containing an organic electrolyte. A poly(cyanogen) (PCN) having the structure $[C(CN){=}N]_n$ is obtained with a molecular weight of approximately 5000. Because the reaction involves formation of the heterocyclic anion

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Table I
Carbon Fibers from Poly(cyanogen)

HTT,[a] °C	time at HTT,[b] h	$10^5\rho_{300}$,[c] Ω m	ρ_{77}/ρ_{300}	E_a,[d] eV
700	12	1000	10.0	0.021
700	36	9	2.1	0.007
900	12	8	1.4	0.003
900	12	7	1.2	0.002
1000	36	3.1	1.20	0.002
1000	36	2.5	1.16	0.001
1500	4	1.7	1.07	0.0007
1500	4	1.7	1.04	0.0004

[a] Heat treatment temperature. [b] The furnaces were brought to the HTT in <10 min, with the exception of the 1500 °C experiments, where the furnace was preheated prior to sample insertion. [c] Resistivity at 300 K. [d] From $\rho = \rho_0 \exp(E_a/kT)$.

$C_7N_7^-$,[2,3] followed by its formation of an open-structured dimer,[3] the polymer is *not* an ordered chain but contains some C–C and N–N links as well in the backbone. In analogy to the well-known conversion of poly(acrylonitrile) (PAN) to carbon fibers,[4] this polymer might be expected to form a carbon network, perhaps incorporating more nitrogen into the structure than would be encountered in PAN-based fibers. In this communication, we wish to report successful formation of PCN fibers, their conversion to carbon fibers at temperatures up to 1500 °C, and their conducting properties.

PCN of approximately 5000 molecular weight was prepared in a single-chambered argon-purged electrochemical cell. $(CN)_2$ (1.2 M) in acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate was subjected to 9 V dc at an initial current of 60 mA for 48 h using glassy carbon electrodes. Polymer forms at the anode and flakes off into the cell. The yield of PCN is typically approximately 45% of the $(CN)_2$ employed. A small amount of oxidation is encountered, and the C/N ratio is approximately 1.2; however, NMR spectroscopic evidence indicates no significant incorporation of the solvent acetonitrile into the polymer.[1] A typical analysis of PCN is as follows: % C, 49.2; % N, 44.8; % H, 2.8; % O, 1.5.

Solutions of PCN in tetrahydrofuran (THF) are prepared by stirring approximately 10% polymer in THF overnight. Solvent is evaporated until the polymer concentration is 35–40% by weight. From this deep brown viscous solution, it is possible to draw fibers with a pipet by pulling slowly. Lengths of 10 in. or more are easily drawn with fiber sizes from a few micrometers to 50 μm. All these operations are performed in an argon-purged glovebox.

These flexible fibers show distinct uniaxiality when viewed between crossed polars on an optical microscope. Scanning electron microscopy reveals good uniformity of the fibers (Figure 1). By placing them in quartz tubes in vacuo or in ceramic tubes in an argon atmosphere, they may be heated to various temperatures. They retain their morphology (Figure 1) and strength. To date we have studied electrical properties of heat-treated samples to temperatures of 1500 °C. X-ray studies and mechanical testing are in progress.

Thermogravimetric analysis of PCN heated to 1000 °C was performed on a Perkin-Elmer TGS-2. PAN shows a weight loss of 60–67% under these circumstances, whereas rayon shows a weight loss of 87–89% when carbonized to 1000 °C.[5] PCN shows a weight loss of 67% to 1000 °C. The C–N ratio at 700 °C is 5:1 and at 900 °C is 10:1. Table I is a summary of the electrical resistivity data. A standard four-probe dc technique was employed on carbon fibers mounted utilizing conducting silver paint. Temperature-dependent resistivity measurements were performed between 77 and 298 K by inserting the sample block in a liquid nitrogen Dewar flask.

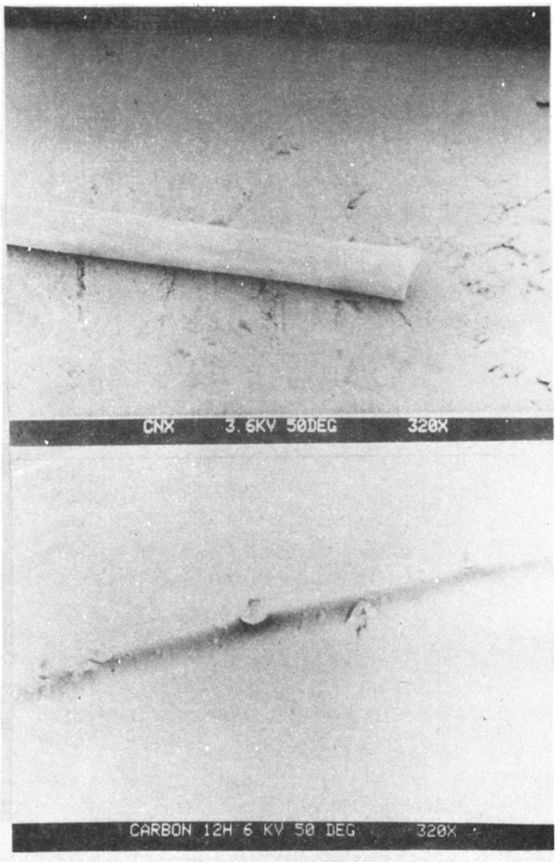

Figure 1. Scanning electron micrographs of fibers. Upper photograph, poly(cyanogen) drawn from THF. Lower photograph, carbon fiber derived by heating at 700 °C.

The low band gaps observed in PCN carbonization are atypical of carbon fibers, while the resistivities are similar to those observed in fibers produced from PAN, pitch mesophase, or benzene decomposition.[6] Because of the simplicity employed in the heat treatment procedure for PCN and the achievement of considerable conductivity at temperatures as low as 700 °C, this new route to carbon fibers seems attractive. Further work in elucidating the mechanical and electrical properties is under way, including treating at higher HTT's.

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References and Notes

(1) J. H. Chen and M. M. Labes, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 517 (1985).
(2) D. W. Wiley, O. W. Webster, and E. P. Blanchard, *J. Org. Chem.*, **41**, 1889 (1976).
(3) V. Skarda, D. Ivkovich, and M. M. Labes, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 107 (1985).
(4) See, for example, J.-B. Donnet and R. C. Bansal, "Carbon Fibers", Marcel Dekker, New York, 1984, p 12.
(5) H. M. Ezekiel and R. G. J. Spain, *J. Polym. Sci., Part C*, **19**, 249 (1967).
(6) J. S. Murday, D. D. Dominguez, J. A. Moran, Jr., W. D. Lee, and R. Eaton, *Synth. Met.*, **9**, 377 (1984).

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