Table 1. Solar x-ray spectrum recorded by Bragg spectrometer.

Wavelength observed (Å)	Lab. meas. or prediction (Å)	Intensity above atm (10^4 photons $cm^{-2} sec^{-1}$)	Element	Transition	Notes
13.7	13.820	1.4	Fe XVII	$2p\ ^1S_0$–$3p'\ ^1P_1$	Possibly also Ne IX. Narrow.
15.0	15.012	11.7	Fe XVII	$2p\ ^1S_0$–$3d\ ^3D^1$	Narrow.
15.25	15.261	7.2	Fe XVII	$2p\ ^1S_0$–$3d\ ^1P_1$	Narrow.
16.0	16.006	4.2	O VIII	$1S\ ^2S_{1/2}$–$3p\ ^2P_{3/2,\ 1/2}$	Lyman β. Narrow.
16.72	16.774	11.1	Fe XVII	$2p\ ^1S_0$–$3s\ ^1P_1$	Narrow.
17.01 and 17.05	17.051	14.7	Fe XVII	$2p\ ^1S_0$–$3s\ ^3P_1$	Doubled by excursion of pointing control. Both peaks narrow.
17.65 and 17.72	17.768	21.0	O VII	$1s^2\ ^1S_0$–$1s4p\ ^1P_1$	Doubled by pointing control excursion.
18.54 and 18.61	18.627	30.0	O VII	$1s^2\ ^1S_0$–$1s3\mathrm{p}\ ^1P_1$	Doubled by pointing control excursion.
18.8 and 18.9	18.969	23.2	O VIII	$1s\ ^2S_{1/2}$–$2p\ ^2P_{3/2,\ 1/2}$	Lyman α. Doubled. Broad wings.
20.8	20.910		N VII	$1s\ ^2S_{1/2}$–$3p\ ^2P_{3/2,\ 1/2}$	Lyman β. Very weak line.
21.55	21.602	461.0	O VII	$1s^2\ ^1S_0$–$1s2p\ ^1P_1$	Broad.
21.70	21.804	212.0	O VII	$1s^2\ ^1S_0$–$1s2p\ ^3P_1$	Broad.
23.2		31.2			Broad. Unidentified. Possibly N VI.
24.8	24.781	85.2	N VII	$1s\ ^2S_{1/2}$–$2p\ ^2P_{3/2,\ 1/2}$	Lyman α. Broad.

tensities. The intensities are given in numbers of photons per square centimeter per second in each line above the earth's atmosphere.

These intensities have been computed from the observed fluxes and the measured spectrometer efficiency. The estimated accuracy is ± 50 percent. In Table 1, four groups of two lines each are shown bracketed. These are single lines that were doubled by pointing excursions which interrupted the continuity of the spectrometer scan.

The narrow widths of the lines of Fe-XVII, indicate that they originate in active regions of approximately the same dimensions as plages. The Lyman β line of O VIII is also narrow, but the lines of O VII and N VII are as broad as would be expected from a source covering the full disk.

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Notes

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Electroconductive Polymers

Abstract. *Polymers of a new type with an unusual combination of properties have been synthesized. They are of high molecular weight, they are soluble in organic solvents, and they can be cast as films. Their electrical conduction is electronic in the solid state and can be controlled up to a conductivity of 10^{-3} ohm^{-1} cm^{-1}.*

That electroconductive organic polymers possessing the mechanical properties of the common insulating plastics have potential value is attested by the numerous reported attempts at synthesis. The work from previous years has been reviewed (*1*). The more recent contributions (*2*) deal with the synthesis of conductive polymers by introducing conjugation, free radicals, charge transfer complexes, or metal ions as part of a polymeric structure and, more empirically, by pyrolysis of otherwise nonconductive materials. The resulting products have been either insoluble, infusible powders or, if soluble, of low molecular weight, low conductivity, or both (*3*). We now report preliminary studies of a class of electroconductive polymers, of high molecular weight, that can be deposited from solution as homogeneous films suitable for making physical measurements.

Microcrystalline, monomeric salts of the tetracyanoquinodimethane anion (TCNQ$^-$) and related complex anions —for example, (TCNQ)$^-_2$—possess conductive properties (*4*). Our observations are that combinations of these ions with polymeric cations produce polymers that can readily be cast as coherent films and have electric conductivities as high as 10^{-3} ohm^{-1} cm^{-1} (*5*).

Poly(2-vinylpyridine), molecular weight 2.2×10^6, was alkylated with excess dimethylsulfate in alkaline solution. The resulting poly(1-methyl-2-vinylpyridinium methylsulfate) (*6*) was freed of inorganic salts by dialysis and was shown by titration to be completely *N*-alkylated. A solution of this polymer in 50 percent ethanol, well stirred under nitrogen, was mixed with a solution of the lithium salt of TCNQ in 50 percent ethanol, the amount of TCNQ being sufficient to provide one TCNQ anion for every monomer unit. The precipitate formed was collected, washed with aqueous ethanol, washed repeatedly with ethanol, and dried in a vacuum over phosphorus pentoxide. Films of this material were cast from dimethylformamide or acetonitrile and cut into shapes appropriate for four-point probe measurement of conductivity; silver electrodes were painted on as contacts. Conductivity of these films was markedly dependent on the presence of neutral TCNQ, which was added, in these studies, to the solutions from which the films were cast (Table 1).

A copolymer of styrene and 2-vinylpyridine (molecular weight greater than 5×10^4) containing 45 mole percent vinylpyridine residues was alkylated with *n*-butyl iodide in a mixture of ethyl acetate and nitromethane. Analysis of the ether-precipitated polymer indicated that 80 percent of possible quaternization had occurred. Th product was allowed to react wit slightly more than the stoichiometri quantity of lithium TCNQ in aqueo ethanol, under nitrogen, and the pr

Table 1. Conductivity of poly(1-methyl-2-vinylpyridinium TCNQ) films.

Neutral TCNQ (% by wt)	$\sigma_{300^\circ K}$ (ohm^{-1} cm^{-1})
0	$> 10^{10}$
2	$> 10^{10}$
5	3.3×10^{-6}
15	1.0×10^{-4}
22	1.7×10^{-4}
40	1.1×10^{-5}

Table 2. Conductivity of copoly(styrene,1-butyl-2-vinylpyridinium-TCNQ) films.

Neutral TCNQ in films (% by wt)	$\sigma_{300^\circ K}$ (ohm^{-1} cm^{-1})
0	$> 10^{10}$
3	1.0×10^{-10}
6	1.3×10^{-9}
10	6.5×10^{-5}
15	1.1×10^{-3}
20	1.1×10^{-4}
25	1.0×10^{-4}
30	1.3×10^{-5}

cipitated salt was washed repeatedly with ethanol before drying in a vacuum over phosphorus pentoxide. Analysis indicated that seven-eighths of the iodide anions had been replaced by TCNQ$^-$. Films of this product were cast from dimethylformamide. Again conductivity was strongly dependent on the presence of added neutral TCNQ (Table 2).

Results similar to these two have been obtained with quaternized derivatives of other basic polymers, including poly(1-vinylimidazole), poly(4-dimethylaminostyrene), poly(ethyleneimine), poly(4-vinylpyridine), as well as with incompletely quaternized samples of poly(2-vinylpyridine). In all cases the conduction behavior is similar to that just described, ranging from less than 10^{-10} to 10^{-3} ohm^{-1} cm^{-1}, depending on the neutral TCNQ content of the polymer films. The conduction process is electronic, as demonstrated by experiments in which polarization or electrolytic effects have been shown to be absent after the passage of large amounts of charge. The conductivity as a function of temperature can be described by the expression $\sigma = \sigma_0 e^{-E/kT}$. Experimentally determined activation energies in the presence of added TCNQ are of the order of 0.1 to 0.3 ev.

Those TCNQ-containing films having relatively good conductivity, that is, approximately 10^{-5} ohm^{-1} cm^{-1}, have a matte surface and in several cases have been shown by x-ray diffraction to possess a degree of order that does not result from crystallites of neutral TCNQ; in systems having poly(2-vinylpyridine) as the basic unit, this order corresponds to a 6.3-Å spacing. Except at very high concentrations (more than 20 percent), there is no evidence of crystalline neutral TCNQ in the conductive films. The coincidental appearance of regularity with a sharp increase in conductivity over a narrow TCNQ concentration range strongly indicates that ordered structures play an essential part in the conduction process.

The maximum conductivity of the TCNQ-doped films of the various polymers examined lies in the region 10^{-3} to 10^{-5} ohm^{-1} cm^{-1}, regardless of the polymeric cation; the narrowness of this range suggests that the polymer backbone and side chains do not participate directly in charge transport.

In studies of crystalline ammonium and imonium salts of TCNQ$^-$ and (TCNQ)^-_n ions it has been observed that conductivities of the complex salts are usually 10^5 to 10^7 times those of the simple salts (*4*). It is tempting to conclude that conduction in our polymeric TCNQ derivatives is associated with contiguous ordered regions in which the conduction process is related to that in the complex salts. It can be determined from Tables 1 and 2, however, that the overall ratio of neutral TCNQ to its radical anion in our most effectively conductive films is considerably less than unity, the value that would correspond to the (TCNQ)$^-_2$ ion.

Combination of the TCNQ radical anion with the cationic groups of most of the polymers we have prepared to date is apparently not stoichiometric.

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References and Notes

1. F. X. de Charentanay, P. Castel, P. L. Teyssie, *Polymères, Semi-Conducteurs* (Institut Français du Pétrole, May 1963); J. H. Kallweit, *Kolloid-Z*, **188**, 97 (1963); L. T. Yu, *J. Phys. Radium* **24**, 330 (1963).
2. D. Chapman, R. J. Warn, A. G. Fitzgerald, A. D. Yoffee, *Trans. Faraday Soc.* **60**, 294 (1964); J. E. Keaton and B. S. Wildi, *J. Chem. Phys.* **40**, 2977 (1964); G. P. Brown and S. Aftergut, *J. Polymer Sci.* **A2**, 1839 (1964); M. J. S. Dewar and A. M. Talati, *J. Amer. Chem. Soc.* **85**, 1874 (1963); **86**, 1592 (1964); A. Mizoguchi, H. Moriga, T. Shimizu, Y. Amano, *Natl. Tech. Rept.* (Matsushita Elec. Ind. Co., Osaka) **9**, 407 (1963); Chem. Abstracts (1964) p. 14626^d; S. B. Mainthia, P. L. Kronick, H. Ur, E. F. Chapman, M. M. Labes, Amer. Chem. Soc. 144th meeting (Los Angeles, Calif.) Abstracts **11Q** (1963).
3. A. A. Berlin, B. I. Liogonsky, V. P. Parini, *Izv. Akad. Nauk SSSR*, 705 (1964); H. A. Pohl and R. P. Chartoff, *J. Polymer Sci.* **A2**, 2787 (1964); M. Benes, J. Peska, O. Wichterle, *J. Polymer Sci.* **C4**, 1377 (1963).
4. L. R. Melby, R. J. Harder, W. R. Hertler, R. E. Benson, W. E. Mochel, *J. Amer. Chem. Soc.* **84**, 3374 (1962).
5. M. Hatano, H. Nomori, and S. Kambara described similar compounds at the Amer. Chem. Soc. 148th meeting (Chicago, September 1964). See *Reports on Progress in Polymer Physics in Japan I* (1964), p. 321; *Polymer Preprints* (Amer. Chem. Soc., September 1964), p. 849.
6. Poly(vinyl-*N*-alkylpyridinium) ions were first described by R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.* **3**, 246 (1948).
7. We thank J. J. Hertz for assistance with the electric measurements and J. R. Ladd for supplying TCNQ. Paper presented at the Amer. Chem. Soc. 148th Meeting.
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Osmiophilic Reagents: New Cytochemical Principle for Light and Electron Microscopy

Abstract. *Established histochemical procedures have been altered by utilizing reagents which contain a group capable of reacting selectively with OsO_4. This permits the cytochemical demonstration of a particular enzyme or functional group of a macromolecule with the light and electron microscope. The osmiophilic groups used thus far are mercapto, thiocarbamyl, and diazothioether. The "osmium black" produced at the site of reaction is electron opaque, is insoluble in lipids, and is not altered when the issue is embedded in acrylic and epoxy resins. Its fine amorphous character enables it to be maintained precisely in the electron beam.*

To use the electron microscope in cytochemistry, it is important to find reagents that will not only react selectively with the specimen to be viewed but increase the electron opacity at the site of a particular enzyme or functional group of the specimen and hence improve the contrast of the image. Reagents which contain elements of high mass density as well as high atomic number (*1, 2*), or have the ability to combine after the tissue reaction with