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MIXED VALENCE, SEMICONDUCTING FERROCENE - CONTAINING POLYMERS

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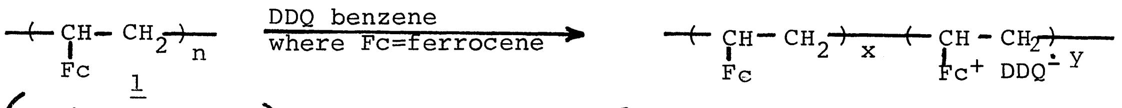
Both conjugated and nonconjugated ferrocene polymers were partially oxidized by DDQ, TCNQ, and I_2 to give mixed valence semiconducting polymers.

Organic polymers are usually insulators, but highly conjugated polymers[2] and organic charge-transfer complexes[3] can be semiconducting. Recently, tetracyanoquinodimethan (TCNQ) salts of tetrathiafulvalene[4] and bisfulvalenediiron[5] were found to be metallic ($\sigma = 10^1$ to $10^3 \Omega^{-1} cm^{-1}$ with a negative temperature coefficient). We reasoned that introducing mixed valence states, together with extended conjugation, might induce polymers to be semiconductors. Furthermore, the simultaneous presence of both factors might synergistically enhance conductivity. We were encouraged by the observations of Cowan and Kaufman[6] demonstrating the conductivity of biferrocene Fe(II)Fe(III) picrate was six orders of magnitude greater than either biferrocene or biferrocene Fe(III)Fe(III) dipricate. Thus, model ferrocene-containing polymers were converted into Fe(II)Fe(III) complexes in this study.

Polyvinylferrocene,[7] 1, polyferrocenylene,[8] 2, and polyethynylferrocene,[9] 3, were prepared and purified. Then, each was oxidized by dichlorodicyanoquinone (DDQ), iodine, and TCNQ to give a series with a range of Fe(II)/Fe(III) ratios. The percent oxidation was controlled by the reactant stoichiometry, and Fe(II)/Fe(III) ratios were established, both by elemental analyses and by Mössbauer spectroscopy.[10] In each case the isomer shifts and quadrupole splittings were about 0.78 mm sec^{-1} and 2.48 mm sec^{-1} for ferrocene units and about 0.78 and 0.0 to 0.2 for ferricenium units. Each DDQ molecule incorporated into the polysalts was reduced to $DDQ^{\dot{-}}$ as evidenced by the absence of 1680 $cm^{-1} \nu_{CO}$ of DDQ and the presence of the 1590 $cm^{-1} \nu_{CO}$ of $DDQ^{\dot{-}}$.[10] The Fe(II)/Fe(III) ratios from elemental analyses agreed within ±5% of those determined by Mössbauer. All mixed valence polymers were blue-black or balck due to the ferricenium 620 nm $^2E_{2g} \rightarrow {}^2E_{1u}$ transition. Polysalts of 2 had a broad electron-transfer band[6,11] at 1100-1900 nm.

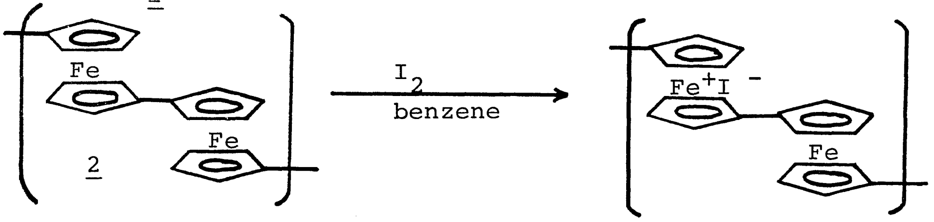
Oxidation of 2 with TCNQ was successfully carried out in nitrobenzene or benzonitrile (but not in benzene, THF, or CH_2Cl_2) at 50-90°. Only 1:1 complexes could be obtained (each ferricenium unit generated was associated with $TCNQ^{\cdot-}$). However, under these conditions polyvinylferrocene gave only charge-transfer complexes with TCNQ which exhibited no ferricenium absorption in the Mössbauer spectrum. TCNQ could be continuously extracted from these complexes with benzene. No success was achieved in preparing polysalts of 1, 2, or 3 where $(TCNQ_2)^{\cdot-}$ groups were incorporated for each ferricenium unit.

(1)

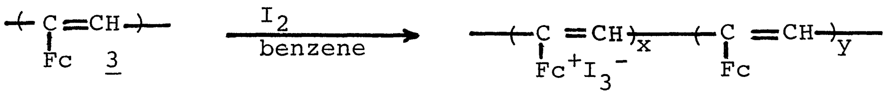


$$-(\underset{Fc}{CH}-CH_2)_n- \xrightarrow[\text{where Fc=ferrocene}]{\text{DDQ benzene}} -(\underset{Fc}{CH}-CH_2)_x-(\underset{Fc^+\ DDQ^{\cdot-}}{CH}-CH_2)_y-$$

(2)



(3)



$$-(\underset{Fc}{C}=CH)- \xrightarrow[\text{benzene}]{I_2} -(\underset{Fc^+I_3^-}{C}=CH)_x-(\underset{Fc}{C}=CH)_y-$$

Compressed pellets of the polysalts (0.6 to 1.0 mm thick) were made, and their conductivities were obtained, as described,[11] at 200V. Plots of conductivity versus the percent Fe(III) are shown in figures 1 and 2. Several conclusions are apparent. (1) Polymers 1, 2, and 3 are insulators with $\sigma = 8\times10^{-15}$, 1.2×10^{-14}, and 4.5×10^{-14} $\Omega^{-1}cm^{-1}$ respectively. A previous report[12] that the conductivity of 3, prepared from acetylferrocene in $ZnCl_2$, was 10^{-10} $\Omega^{-1}cm^{-1}$ must have involved a polymer that was partially oxidized or contained metallic impurities. To get accurate values, polymers 1-3 must be reduced prior to compaction to avoid small amounts of ferricenium incorporation. (2) Upon partial oxidation, all three become semiconductors. Small percentages of oxidation cause large increases in conductivity. (3) For all samples, conductivity maximized between 35 to 65% Fe(III), and in this region the curves are not steep. (4) Conductivity increases of six to eight powers of ten were achieved, but to a first approximation the conductivities were independent of the anion present. (5) Increasing conjugation (going from complexes 1 to those of 3) did not markedly effect the conductivity. Thus, no synergism existed between extended conjugation and mixed valence states in these samples. These observations are consistant with an electron-hopping model where ferrocene is surrounded by a maximum number of nearest neighbor ferricenium moieties. None of the polysalts exhibited photoconductivity. Under 200W and 500W tungsten lamp irradiation the conductivities were essentially unchanged. Conjugation in 2 or its polysalts could be interrupted by occasional serious tilting of adjacent ferrocene units with respect to each other, although the preferred conformation is the staggered structure shown in equation 2 where conjugation is possible. It is known from Mössbauer,[10] uv,[6] and magnetic susceptibility studies[13] that the positive charge in ferricenium and biferrocene [Fe(II)Fe(III)] is largely localized on iron. Thus, "conjugative assistance" of electron transfer through the π-system, even in polysalts of 3, has no appreciable effect on bulk conductivity.

FIGURE 1. CONDUCTIVITY OF MIXED-VALENCE DDQ POLYMERS

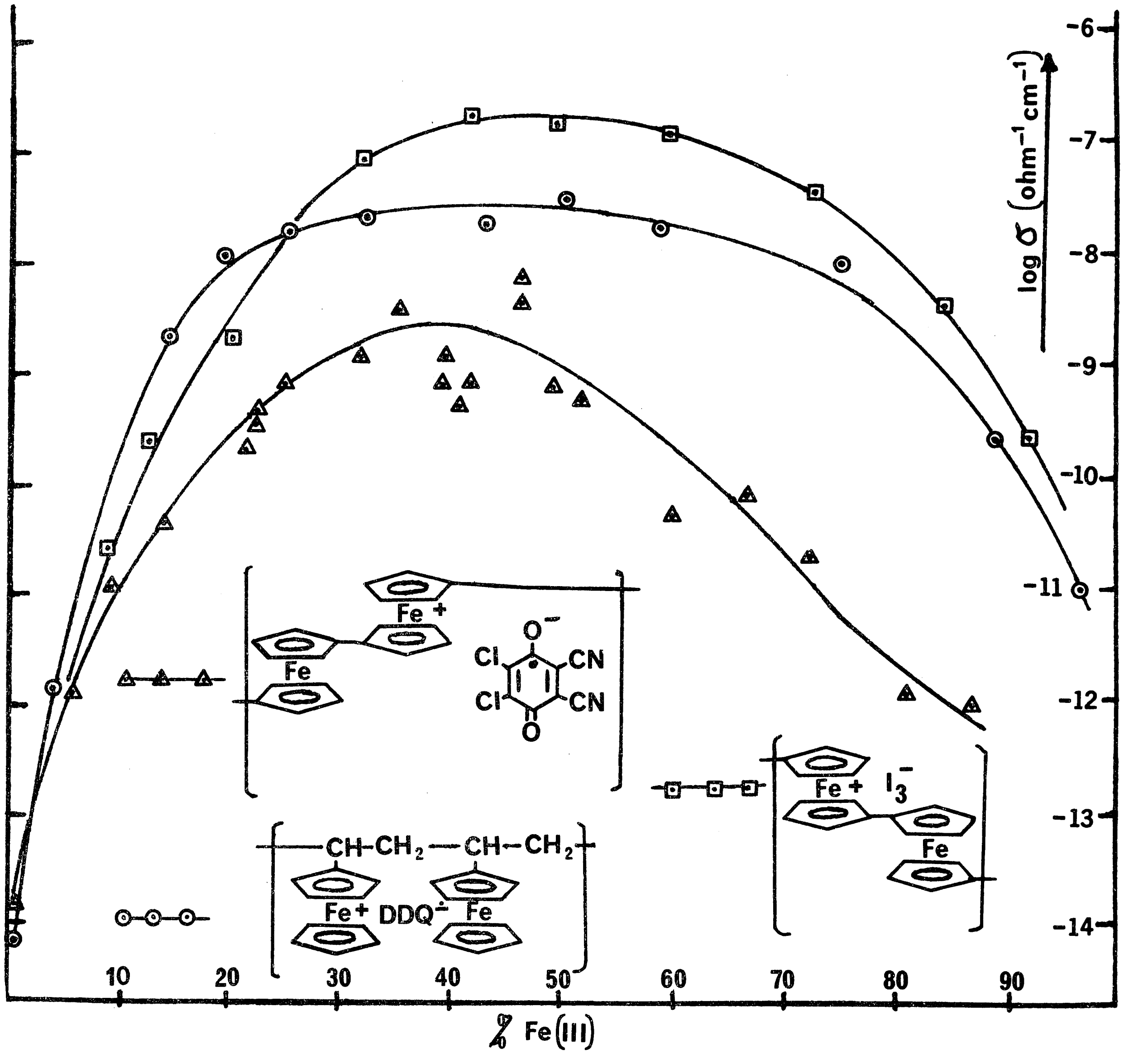
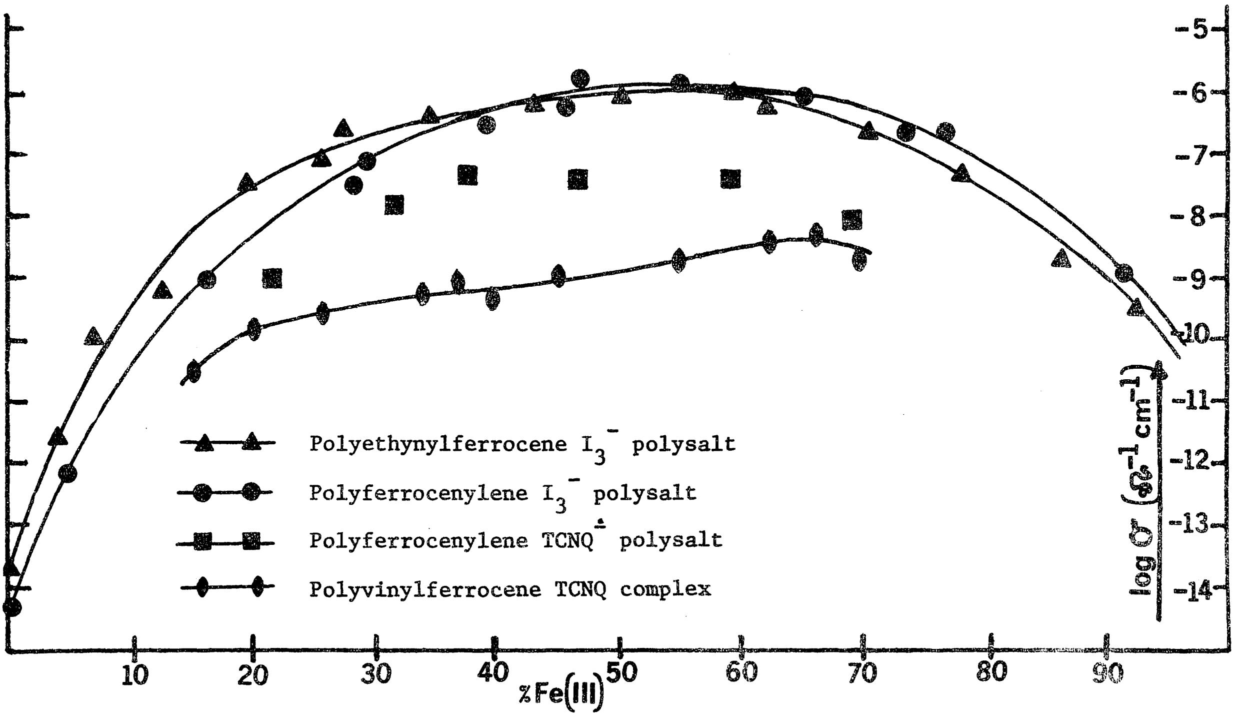


FIGURE 2. CONDUCTIVITY OF MIXED VALENCE FERROCENE POLYMERS



REFERENCES

1. The authors thank the Office of Naval Research and the Air Force Cambridge Laboratory (contract number F-1968-71-C-0107) for support of this work.

2. W. A. Little, "Superconductivity of Organic Polymers," in Electrical Conduction Properties of Polymers, J. Polymer Sci., C, 17 (1967).

3. R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York (1969).

4. For a review see A. F. Garito and A. J. Heeger, Accounts Chem. Res., 7, 232 (1974).

5. D. O. Cowan and C. LeVanda, ibid., 94, 9271 (1972).

6. D. O. Cowan and F. Kaufman, ibid., 92, 219 (1970); F. Kaufman and D. O. Cowan, ibid., 92, 6198 (1970).

7. Y. Sasaki, L. L. Walker, E. L. Hurst, and C. U. Pittman, Jr., J. Polymer Sci.-Chem., 11, 1213 (1973).

8. N. Bilow, A. L. Landis, and H. Rosenberg, ibid., A-1, 7, 2719 (1969).

9. C. U. Pittman, Jr., Y. Sasaki, and P. L. Grube, J. Macromol. Sci.-Chem., A8(5), 923 (1974).

10. C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prados, Macromolecules, 3, 746 (1970).

11. D. O. Cowan, J. Park, C. U. Pittman, Jr., Y. Sasaki, T. K. Mukherjee, and N. A. Diamond, J. Amer. Chem. Soc., 94, 5110 (1972).

12. Ya. M. Paushkin, T. P. Vishnyakova, L. S. Polak, I. I. Patalah, F. F. Macius and T. A. Sokolinskaja, Visokomol Soed., 6, 545 (1964); J. Polymer Sci. Part C, 4, 1481 (1964).

13. D. O. Cowan, G. A. Candela, and F. Kaufman, J. Amer. Chem. Soc., 93, 3889 (1971).

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