

Iron(III) Perchlorate Doping of Polyacetylene

John R. Reynolds,^a James C. W. Chien,^{*a,b} Frank E. Karasz,^a C. Peter Lillya,^b and D. J. Curran

^a Polymer Science and Engineering Department, and ^b Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, U.S.A.

Free-standing films of polyacetylene have been oxidized with $\text{Fe}(\text{ClO}_4)_3$ to yield materials exhibiting high electrical conductivity thus providing an alternative route to the electrochemical p-doping with perchlorate anion.

The chemical and electrochemical oxidation or reduction (p- and n-type doping) of the extended π system of polyacetylene $(\text{CH})_x$ has been the focus of much attention because the nearly dielectric polymer can be converted into an organic metal with an increase in conductivity of up to 13 orders of magnitude.^{1,2} Transition metal compounds have been used as p-type dopants, but previous methods leave the transition metal in the polymer as either the dopant species (*e.g.* FeCl_3)³ or as the reduced metal (*e.g.* AgClO_4).⁴ This work describes the oxidation of $(\text{CH})_x$ with $\text{Fe}(\text{ClO}_4)_3$ to give electrically conducting films with a chemical composition of $[(\text{CH})(\text{ClO}_4)_y]_x$. This composition is the same as that found when using $(\text{CH})_x$ as the anode in electrochemical doping with perchlorate salts as electrolyte.⁵

Polyacetylene films, prepared by the method of Ito *et al.*,⁶ were doped by immersion in saturated solutions of anhydrous $\text{Fe}(\text{ClO}_4)_3$ in dry toluene with stirring. After doping to the desired conductivity, the films were removed, washed thoroughly with toluene and CH_2Cl_2 , then dried *in vacuo* overnight.

The room temperature conductivity for $(\text{CH})_x$ films, doped to saturation with $\text{Fe}(\text{ClO}_4)_3$, is greater than $500 \Omega^{-1} \text{cm}^{-1}$. The undoped films are silver in colour and upon doping turn a brilliant gold. The conductivity increase can be monitored with time, reaching its limiting value after 2–3 h, when the dopant has diffused completely into the film. Interestingly, experiments carried out in either MeOH or H_2O as the solvent

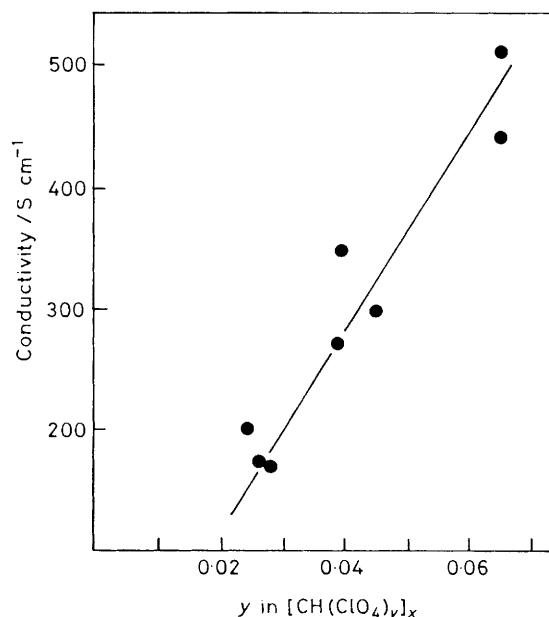
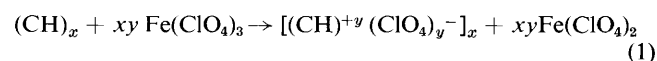


Figure 1. Dependence of conductivity on dopant level.

were unsuccessful. The solvated $\text{Fe}(\text{ClO}_4)_3$ does not diffuse into the polymer probably because of the increased molecular size or a preference to remain in the polar medium.

Figure 1 shows the dependence of conductivity on dopant level from 2 to 6.5 mol % as determined by weight uptake. The conductivity can be controlled by controlling the dopant level, though at low levels the dopant distribution is probably inhomogeneous owing to incomplete diffusion. The reproducibility of the data is shown for different experiments.

Elemental analyses of a doped film indicate a chemical formula of $\text{C}_{1.00}\text{H}_{1.04}\text{Cl}_{0.0032}\text{O}_{0.092}$ where the oxygen content is obtained by difference. The theoretical constitution of $[\text{CH}(\text{ClO}_4)_{0.025}]_x$ as determined by weight uptake is: C 77.5, H 6.5, Cl 5.7, O 10.3, Fe 0.0%; Found: C 76.6, H 6.6, Cl 7.4, O 9.4, Fe <0.05%. The Fe content is less than 6.5×10^{-5} moles of Fe per mole of carbon indicating that the dopant species is not a transition metal complex. The doping reaction occurs by the mechanism (1).



The e.s.r. spectrum of undoped $(\text{CH})_x$ shows a narrow line near the absorption of the free electron ($g = 2.0023$). Doping to a composition of $[\text{CH}(\text{ClO}_4)_{0.045}]_x$ with $\text{Fe}(\text{ClO}_4)_3$ gives a line near the same g value but assumes a Dysonian shape⁷ with an A:B ratio of 8:1 consistent with metallic electrons. We have observed very similar lineshapes for $(\text{CH})_x$ samples doped electrochemically with ClO_4^- . The calculated skin depth of 29 μm for films with a conductivity of $300 \Omega^{-1} \text{cm}^{-1}$ is less than

the 100 μm thickness of our films, consistent with these results.

One further piece of evidence demonstrating the metallic nature of these films is thermoelectric power data. We have found a low value of $+30 \mu\text{V}/\text{K}$ for a film with a composition of $[\text{CH}(\text{ClO}_4)_{0.065}]_x$ as expected for a material exhibiting high electrical conductivity. The positive sign of the voltage measured shows the p-type nature of this dopant.

The mechanisms of this doping reaction lead to the same material as that produced in anodic oxidation and will be of use in further electrode and battery studies.

This work was supported in part by grants from the N.S.F., O.N.R., and D.A.R.P.A.

Received, 2nd August 1982; Com. 910

References

- 1 J. C. W. Chien, *J. Polym. Sci., Polym. Lett. Ed.*, 1981, **19**, 249.
- 2 A. G. MacDiarmid and A. J. Heeger, *Synth. Met.*, 1979/1980, **1**, 101.
- 3 A. Pron, I. Kulszewicz, D. Billaud, and J. Przyluski, *J. Chem. Soc., Chem. Commun.*, 1981, 783.
- 4 T. C. Clarke, R. H. Geiss, J. F. Kwak, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 1978, 489.
- 5 P. J. Nigrey, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1979, 594.
- 6 T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 11; 1975, **13**, 1943.
- 7 F. J. Dyson, *Phys. Rev.*, 1955, **98**, 349.