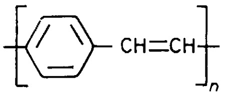
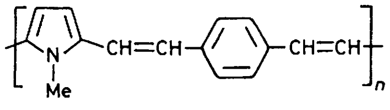
Organic Metals: Poly(*N*-methylpyrrole-2,5-diylvinylene-1,4-phenylenevinylene). A New Polymer of High Electrochemical Reversibility

Kwan-Yue Jen, Michael P. Cava,* Wu-Song Huang, and A. G. MacDiarmid*
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, U.S.A.

Poly(*N*-methylpyrrole-2,5-diylvinylene-1,4-phenylenevinylene) (MPPV), a new conjugated polymer, is rapidly oxidized by iodine to give material having an electrical conductivity of almost 10^{-1} S/cm; cyclic voltammetry of MPPV shows a high degree of electrochemical reversibility which is comparable to that of polyacetylene.



(1)



(2)

Poly(arylene vinylene)s represent a class of conjugated organic polymers which are intermediate in structure between polyacetylene and the polyarylenes, and which are capable of virtually unlimited structural variation as potential new organic metals. It has been shown recently that the readily prepared poly(*p*-phenylene vinylene) [PPV, (**1**)][1] becomes highly conducting after AsF_5 treatment, although it cannot be oxidized by I_2.[2] In contrast, when every other phenylene unit of (**1**) is replaced by a ferrocene unit, the conductivity of the resulting polymer can be increased from $<10^{-12}$ to

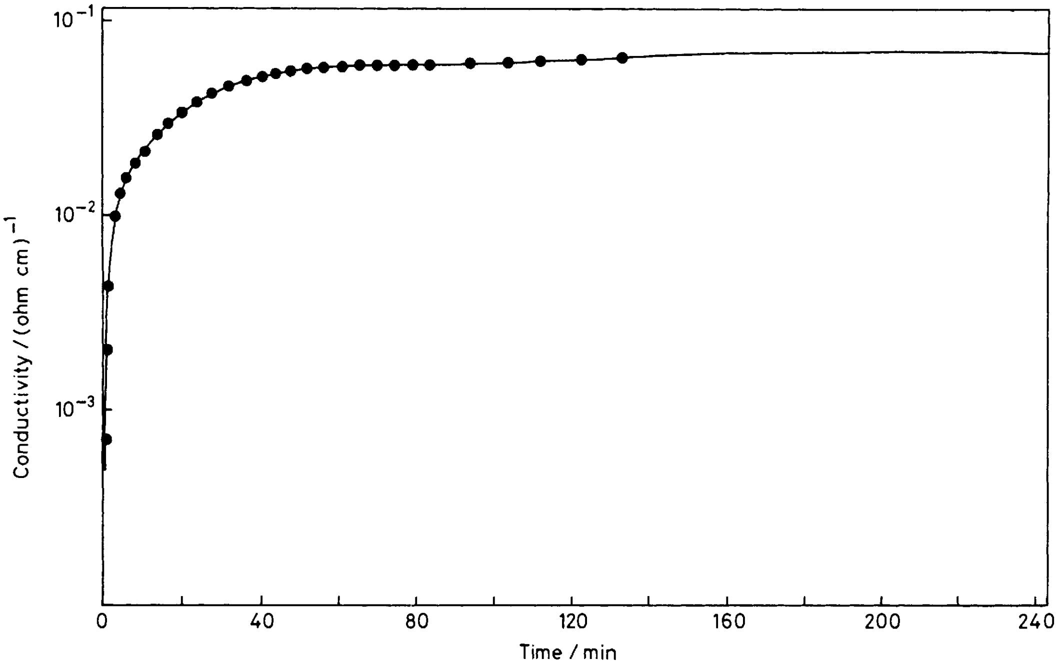


Figure 1. Iodine doping of MPPV, (**2**), *in vacuo* at 25 °C.

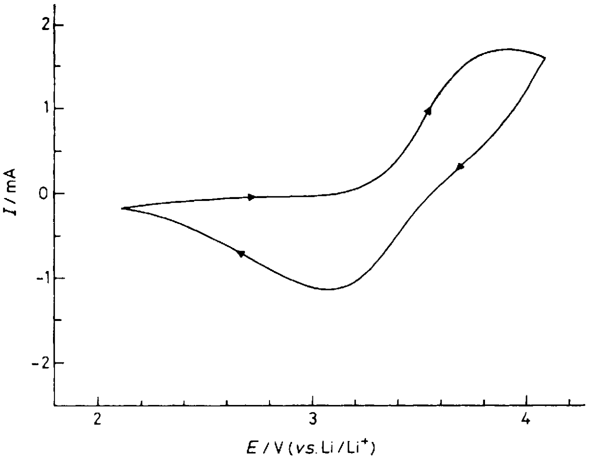


Figure 2. Cyclic voltammogram of MPPV, (**2**).

10^{-4} S/cm by oxidation with I_2.[3] We now report the synthesis and unusual oxidative behaviour of poly(*N*-methylpyrrole-2,5-diylvinylene-1,4-phenylenevinylene) [MPPV, (**2**)], an analogue of (**1**) containing alternate benzene and pyrrole units.

The reaction of tetraethyl 1,4-xylylene diphosphonate[4] (1 equiv.) with Bu^{t}OK (2 equiv.) in *N*,*N*-dimethylformamide, followed by addition of *N*-methylpyrrole-2,5-dialdehyde[5] gave, after overnight heating at 120 °C (N_2), *trans*-MPPV (**2**) as a deep red powder, m.p. >330 °C. Elemental analysis was in accord with an average composition of $n = 4$, with one aldehyde and one phosphonate ester as end groups.

A remarkably rapid conductivity increase of (**2**) was observed when a compressed pellet of the polymer was exposed to I_2 vapour at room temperature (Figure 1). Within five minutes, the conductivity rose from an initial value of 10^{-8} S/cm to over 10^{-2} S/cm, and then slowly levelled off after 12 h to about 10^{-1} S/cm, with a doping composition of $MPPV^{0.85+}(I_3^-)_{0.85}$. Like other conducting polymers,[1] the I_2-doped black material was opaque in the infrared region.

The cyclic voltammetry of MPPV, (**2**) was studied using a three-electrode cell in which the cathodic working electrode consisted of a compressed MPPV pellet embedded in a Pt grid. The counter electrode and reference electrode were both lithium metal, and the electrolyte was 1 M $LiClO_4$ in propylene carbonate. Cyclic voltammograms between 2.1 and 4.1 V (5 mV/s scan rate) revealed an oxidation peak at 3.9 V and a reversible reduction peak at 3.1 V (Figure 2); these values are very similar to those (3.7 and 3.2 V, respectively) shown by polyacetylene.[6] Although the current levels decreased with cycling, the coulombic recovery Q_{in}/Q_{out} was always in the 80—90% range, indicative of a high degree of chemical reversibility comparable to polyacetylene.

The unusual electrochemical properties of MPPV suggest that it, or closely related polymers, may be of considerable interest in organic battery applications.

This work was supported by a grant from the National Science Foundation through the Laboratory for Research on the Structure of Matter and by the Department of Energy.

Received, 14th September 1983; Com. 1227

References

1 R. N. McDonald and T. W. Campbell, *J. Am. Chem. Soc.*, 1960, **82**, 4669.
2 G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, *Polymer*, 1979, **20**, 1441.
3 R. Gooding, C. P. Lillya, and J. C. W. Chien, *J. Chem. Soc., Chem. Commun.*, 1983, 151.
4 P. G. Chantrell, C. A. Pearce, C. R. Toyer, and R. Twaits, *J. Appl. Chem.*, 1965, 460.
5 C. E. Loader, G. H. Barnett, and H. J. Anderson, *Can. J. Chem.*, 1982, **60**, 383.
6 B. L. McKinney and R. C. Burrow, Abstracts of the Electrochemical Society Meeting, San Francisco, California, 1983, p. 844.