

POLYPYRROLE: AN ELECTROCHEMICALLY SYNTHESIZED CONDUCTING ORGANIC POLYMER*

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Summary

The simple, one-step electrooxidation of pyrrole from an organic solvent on a platinum electrode results in the formation of a flexible, metallic polymer. The black films stripped from the electrode are found to be unchanged under ambient storage and thermally stable to temperatures exceeding 300 °C. They are space filling, unlike the fibrillar $(CH)_x$ and show considerable disorder. The room temperature conductivity ranges from 10 - 100 $(\text{ohm cm})^{-1}$. The thermopower is small and positive, decreasing linearly with decreasing temperature, consistent with p-type metallic conduction. The very small Hall constant is anomalous in both sign and magnitude.

Introduction

There is a considerable activity in the study of the electronic behavior of highly conducting polymers. Prior studies have, for the most part, focused on the inorganic polysulfurnitride system $(SN)_x$ [1, 2] and the organic doped polyacetylene system $(CH)_x$ [3, 4]. The magnitudes of the electrical conductivities are summarized in Fig. 1, where the three top curves describe the conductivities of brominated $(SN)_x$, $(SN)_x$, and $(CH)_x$ doped with AsF_5 vapor. The hazards posed by some of these dopants requires that reasonable care be exercised in obtaining these conducting systems. An understanding of the influences of various physical and chemical parameters on the conduction mechanism is central to these studies. It would be desirable to have available for these investigations, polymer systems whose physical and chemical parameters can be varied. Such a variability in physical and chemical

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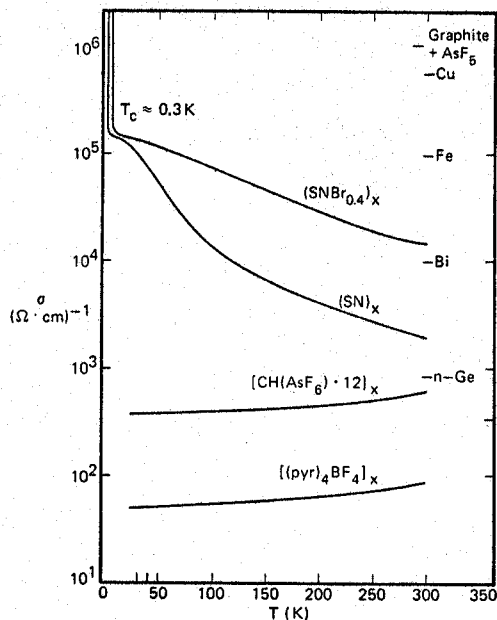


Fig. 1. Conductivity behavior of polypyrrole compared with $(SN)_x$ and $(CH)_x$.

properties would also be required commercially to engineer a flexible conducting polymer. The lowest curve in Fig. 1 shows the conductivity of a new polymeric metal, polypyrrole, which we are presently studying. The room temperature conductivity is in the range of $100 \text{ (ohm cm)}^{-1}$. This film is easily prepared from a simple one-step electrochemical polymerization process, and is mechanically flexible. These films are space-filling and are stable under temperature cycling and ambient storage. They are insoluble and contain no highly hazardous agents. This report describes the electrochemical preparation and initial chemical and physical characterization of these films.

Preparation

A decade ago, Dall'Olio *et al.* [5] had prepared black films of an oxypyrrole by the oxidation of pyrrole on platinum from a sulfuric acid solution. These films were reported to have a room temperature conductivity of 8 (ohm cm)^{-1} . A careful study of the influence of various factors in the electrochemical preparation allowed us to optimize growth conditions where the properties of conductivity, adherence, morphology, and flexibility could all be varied. Some of the variables which were found to influence these properties and which could be controlled in the electrochemical environment are: the electrode material, the solvent, the electrolyte, the oxygen content, the water content, the current density, and the current density history. A quantitative study coupling these variables to the electrical conductivity has

not yet been completed. Some of the correlations which have been observed can be cited, however. Polymerization onto platinum electrodes has been found to result in smoother, better adhering films than when tin oxide electrodes were used. Intrinsic silicon electrodes yielded very poor films, especially regarding uniformity. Films grown from acetonitrile were found to have a higher conductivity than those grown from aqueous solution. Preparations from solutions of deoxygenated organic solvents yielded films which were of somewhat higher conductivity and with less variability, with conductivities between 30 and 100 (ohm cm)⁻¹. The water content in aprotic organic solvents can be used to control the substrate. Absence of water produced very poorly adhering, non-uniform films, and increasing amounts of water improved adherence. Too great an adherence made it difficult to remove the film from the electrode. Excessive current densities yielded films having very rough surfaces. A gradual increase of current from zero to its final value gave films with improved adherence and morphology. Unless otherwise stated, the films whose properties are described here were grown on evaporated platinum electrodes in a single compartment, two electrode electrochemical cell. The counter electrode consisted of gold wire which was tightly wrapped around a glass microscope slide. The cell geometry is illustrated in Fig. 2. The plane parallel structure of the cell arrangement was found necessary to insure thickness uniformity over the film. The cell contained 0.1 M Et₄NBF₄, 0.06 M pyrrole in 99% aqueous CH₃CN. The cell was under galvanostatic control. The cell current was increased linearly with time over a period of three minutes from zero to its final value. The final current density was usually set to 1 mA cm⁻², although values ranging from 0.5 to 1.5 mA cm⁻² were used. Once the final current density was reached, little further change in the cell potential was noted, indicating that the film being deposited was continuing to conduct. The gradual darkening of the platinum electrode as the polypyrrole overlayer increased in thickness could be observed. Films of thickness up to 50 μm were prepared in this manner. These films adhered

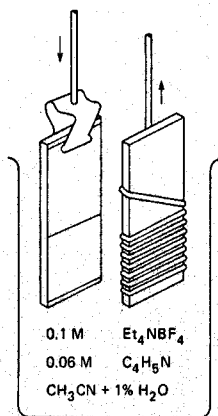


Fig. 2. The single compartment, two electrode cell.

well to the platinum, but by a careful peeling could be removed intact from the surface of the metal.

Film properties

The films removed from the electrode in this manner were flexible, being shiny on the side which had been adjacent to the platinum and matte on the opposite side. Scanning electron micrographs showed a featureless surface on the platinum side and a rough surface of hemispherical hillocks on the opposite side. The interior of the film was found to be compact and, unlike $(\text{SN})_x$ and $(\text{CH})_x$, no evidence of fibrillar structure could be seen. The films exhibit very little structural order, with X-rays showing no discernible peaks and electron diffraction showing weak, diffuse rings. The flotation density of this packed, continuous film was measured to be 1.48 g cm^{-3} . Thermal analysis indicated a small, reversible weight loss of less than 10% below 300°C due, perhaps, to water, and a rapid weight decrease above 600°C .

The film is believed to be a polymer of pyrrole formed by linkages occurring at the α -carbon positions as shown in Fig. 3. This structure has been suggested previously [6] and is supported not only by the structures of pyrrole oligomers but also by the fact that α -substituted pyrrole molecules do not form films. The elemental composition of these films is indicated in the lower portion of the Figure and is consistent with the notion of a polymer formed from pyrrole rings.

There was difficulty in obtaining consistent elemental compositions, a large part of which could be traced to the uncertainty in the fluorine determination. In fact, even the analyses obtained on the salt $(\text{Et}_4\text{NBF}_4)$ were consistently low in fluorine. Although the films which were analyzed were prepared under the conditions described, the elemental composition of the polymer did show some variation. The sum of the C, H and N totalled $72 \pm 1\%$, with extreme values ranging from 70 to 74%. The presence of the fluoroborate anions suggests that the pyrrole units carry a partial positive charge, with the ratio of anion to pyrrole units being about 1:4. Both Raman and ir studies show bands characteristic of the pyrrole ring [7], in support of this model.

From a knowledge of the chemical composition, the weight, and coulometry during film growth, a Faradaic yield of 0.45 ± 0.05 mole per Faraday

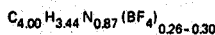
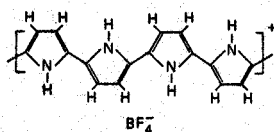


Fig. 3. A possible structure for polypyrrole.

was determined. Using this constant, films of various thicknesses could be prepared.

Electrical behavior

These films showed room temperature conductivities in the range $10 - 100 \text{ (ohm cm)}^{-1}$, although values from 30 to $100 \text{ (ohm cm)}^{-1}$ were most frequently obtained. These films were stable in air, with the conductivity showing no changes after two weeks of ambient storage. Storage over several days under 10^{-5} Torr vacuum did not appreciably change the conductivity. The passage of tens of Faradays of current through a film also left the conductivity unchanged, indicating conductivity of electronic origin.

As suggested earlier, the preparation of polypyrrole could be accomplished under a variety of conditions. The four-probe conductivity of several films grown under different conditions is shown in Fig. 4. The log of the conductivity is plotted against $T^{-0.25}$, as frequently done for disordered conductors. In fact, the behavior of doped $(\text{CH})_x$ has been reported [8] to exhibit this dependence. The upper curve shows the behavior of one film prepared in the manner described in this report, the lower curve shows the behavior of an oxypyrrole polymer grown from a sulfuric acid solution [5]. The film, with room temperature conductivity about 6 (ohm cm)^{-1} , was grown from an aqueous HBr solution, while that with conductivity about 16 (ohm cm)^{-1} was prepared in acetonitrile, on a tin oxide electrode. Several comments are appropriate regarding these curves. It is clear that the temperature dependence of the conductivity is not that of a simple metal, where the conductivity would increase with decreasing temperature. Although the behavior cannot be definitively assigned as a $T^{-0.25}$ process, it is likely that this behavior is indicative of some localization effects arising from disorder. Further, it should be noted that another similarity to $(\text{CH})_x$ exists [8], *viz.*, that the temperature dependence of the conductivity is smaller for samples having larger conductivities.

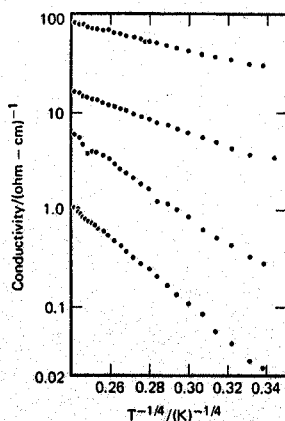


Fig. 4. Log Conductivity vs. $T^{-0.25}$ for several polypyrrole samples.

Using apparatus previously described [9], the thermopower of films of polypyrrole was studied. These results are shown in Fig. 5. At room temperature, the thermopower has the value 6 microvolts $(K)^{-1}$. This value is two or three orders of magnitude smaller than semiconductor values and, in fact, is typical for metallic behavior. It is interesting that the sign of the thermopower is positive, indicating p-type conduction. This is consistent with the notion that the pyrrole polymer is partially oxidized, with the charge compensation being accomplished by the fluoborate anions. Further evidence in support of this was obtained using doping experiments in which the conductivity of films was monitored while they were exposed to various vapors. Exposure to oxidizing AsF_5 and Br_2 vapors gave rise to no significant conductivity change in the film, but exposure to a reducing NH_3 vapor decreased the conductivity of the film by a factor of 15 - 20. This change was largely reversible, the conductivity being nearly restored to within a factor of two of the initial value upon evacuating the sample chamber.

An anomaly in both the sign and magnitude of the Hall constant was noted. For these measurements, a double a.c. technique was used [10]. The temperature dependence of the Hall constant is shown in Fig. 6. The Hall measurement indicated n-type behavior; the Hall constant is anomalously small and only weakly temperature dependent. This behavior is nearly identical with that reported for polyphthalocyanine [11]. This behavior too, suggests a conduction process involving localized states.

By growing polypyrrole on an indium-tin oxide surface in non-aqueous CH_3CN , it was possible to prepare a film of 4 000 Å thickness. By subsequently immersing this electrode in water, it was possible to obtain a free standing film. The absorption constant as a function of incident photon energy is shown in Fig. 7. Corrections have not been applied for reflection or scattering. This spectrum shares two features with that reported [12] on iodine-doped polyacetylene. There is an asymmetric high energy peak and a symmetric low energy peak. In the case of $(CH)_x$, a comparison of the spectra of the doped sample with undoped $(CH)_x$ suggested that the high energy peak was due to interband transitions and that the low energy peak was associated with the conduction electrons. Presently, additional optical studies are in progress to test for this correlation in polypyrrole.

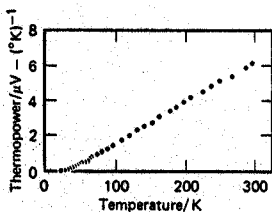


Fig. 5. Thermopower of polypyrrole and its temperature dependence.

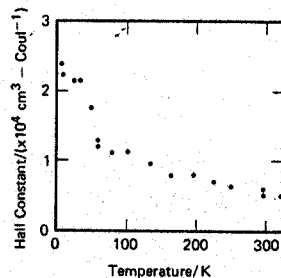


Fig. 6. The Hall constant of polypyrrole as a function of temperature.

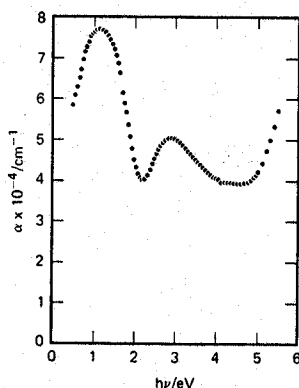


Fig. 7. Absorption coefficient of polypyrrole from 0.5 to 5 eV.

Conclusion

The electrooxidation of pyrrole using a simple one-step process yields a flexible, metallic, organic polymer. The resulting film is dense and compact. It is stable under temperature cycling and under ambient storage. A number of variables are available which can be easily controlled to vary the electrochemical growth environment and, thereby, the resulting physical properties.

There is a chemical flexibility to the pyrrole molecules which can be exploited. For example, polymers of N-Me pyrrole prepared in the same manner show conductivities about five orders of magnitude lower.

This ability to vary the physical and chemical properties of the polymer film represents a significant advantage not only of the polypyrrole system, but also for the electrochemical polymerization method. The properties of the films already obtained for the electrochemically synthesized polypyrrole films represent an important advance over the polyacetylene system with respect to commercial feasibility.

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