Synthesis and Characterization of a Conducting Polymer

An Electrochemical Experiment for General Chemistry

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The electrochemical synthesis of polypyrrole, an electronic conductor in its oxidized form, is an exercise well suited to the general chemistry laboratory. The polymer is a material of considerable contemporary interest (*1*), and its preparation can be used to introduce students to some important principles of electrochemistry and polymer chemistry. Furthermore, the preparation requires only common equipment and inexpensive starting materials. We have found a high level of student enthusiasm for this experiment in our own general chemistry program.

The oxidation and concomitant polymerization of pyrrole is readily effected by either chemical oxidizing agents such as iron(III) salts (*2*) or electrochemical oxidation at an inert electrode (*3*), but only the latter method can produce a freestanding polymer film. In an oxidizing environment pyrrole typically polymerizes by linkage at its alpha positions, along with loss of a proton at each of these positions (Fig. 1). The product thus prepared exists as a positively charged polymer chain that is "doped" with negative ions. The oxidation level is variable, and the half-reaction for for-
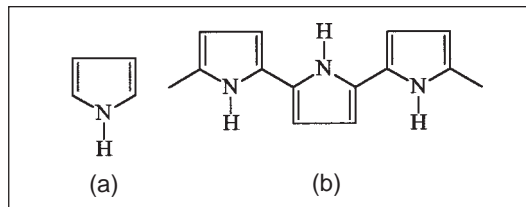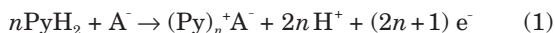

Figure 1. Polypyrrole (a) monomer and (b) polymer chain.

mation of a polymeric unit must therefore be written as shown in eq 1, where PyH_2 = pyrrole and A^- = dopant anion. The value of *n* depends on the precise conditions of the synthesis reaction, and the resultant polymer chain comprises an indefinite number of $(Py)_n^+A^-$ units.

$$n PyH_2 + A^- \rightarrow (Py)_n^+A^- + 2n H^+ + (2n+1) e^- \qquad (1)$$

The number of pyrrole entities per positive charge (*n*) can be determined from the electrochemical data and the mass of polymer produced. The inherently brittle nature of ionic materials can be allayed, to some degree, by the use of a long-chain surfactant such as dodecylbenzenesulfonate as the dopant anion in this polymer.

Experimental Procedure

Synthesis and Stoichiometry

A freestanding, conducting polypyrrole film can be conveniently prepared in a one-compartment cell using stainless steel for anode and cathode. Neither the purity of the reactants nor the quality of the electronic devices is critical

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to the success of the synthesis. In a typical student preparation, electrodes of thin (0.002 in.) stainless steel foil[1] are immersed in an aqueous solution of pyrrole and sodium dodecylbenzenesulfonate (each 0.05–0.10 M) contained in a small beaker. Electrical leads from a dc power supply, with a multimeter in series, are attached to the electrodes. Electrolysis with a current density of 1–2 mA/cm^2 for a period of 30–45 min results in deposition of a smooth film of polypyrrole at the anode. If the anode is weighed before electrolysis, it can be rinsed and dried after deposition to yield the mass of the polypyrrole product. This value, along with the current and time of electrolysis, allows determination of the reaction stoichiometry. There is little difficulty in adjusting to a nearly constant current value throughout the electrolysis procedure.

Calculation from experimental data of the value of *n* in eq 1 is a significant challenge to students at the general chemistry level. The calculation is perhaps most readily handled by equating the number of moles of product expressed in electrochemical terms with the number of moles of product expressed as mass/molecular weight. The relationship is given in eq 2, in which *I* = current (amperes), *t* = time (seconds) and *m* = mass of product (grams). The constants 65 and 325 are, respectively, the formula weights of a pyrrole unit in the polymer and the dodecylbenzene sulfonate anion. The values of *n* thus determined typically fall between 2 and 3.

$$\frac{I \times t}{96,500(2n+1)} = \frac{m}{65n+325} \qquad (2)$$

Electronic Properties of the Product

The generally smooth appearance of the polypyrrole film contrasts with an irregular roughness at the edges of the electrode. To prevent tearing when removing the film from the electrode, it is advisable to trim all four edges of the film and electrode approximately one-eighth inch in from each edge of the polymer. The intact film will then easily slide off the remainder of the electrode.

The relative conductivity of polypyrrole as a function of temperature can be determined with leads attached to a small strip of the polypyrrole film (~0.5 × 2.0 cm) in a test tube immersed in a water bath, as shown in Figure 2. It is advisable to attach the film (e.g., with rubber cement) to a nonconductor such as an acetate sheet (overhead transparency material) to provide additional mechanical strength. A drop of silver paste[2] at each end of the polypyrrole strip will assure a constant degree of electrical contact when leads are clipped to the film. With constant stirring and the hot-plate set at maximum heat, the resistance of the film strip can be recorded at regular temperature intervals as the water bath is heated from room temperature to near boiling. Data from the resistance measurements of poly-
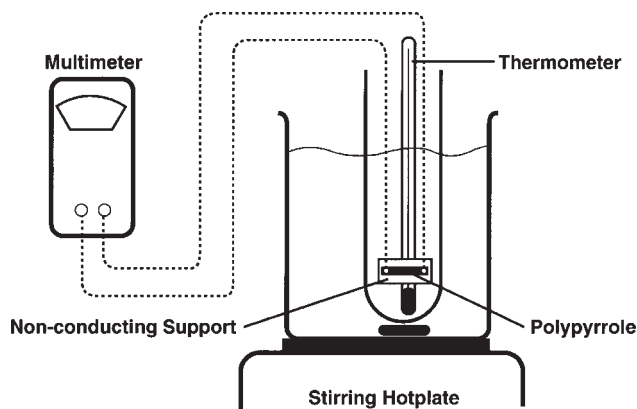
Figure 2. Determination of relative conductance as a function of temperature.

Figure 3. Variation of conductance with temperature of a polypyrrole film.

pyrrole at different temperatures clearly show that the conducting polymer behaves as a semiconductor rather than a metallic conductor. Over the temperature range described, a smooth curve showing decreasing resistance (or increasing conductance) with temperature is easily obtained. A typical curve is reproduced in Figure 3.

Discussion

Owing to its insolubility and intractability, the structure of polypyrrole is not well characterized. The electrochemically prepared material has been shown to be generally anisotropic, with layers of polymer chains parallel to the electrode surface (4), interspersed with layers of the charge-balancing anions (5). The nature of the anion, however, may have a strong influence on the structure and the degree of anisotropy of the polymer (6).

Similarly, the mechanism of electrochemical formation of polypyrrole has not been completely established. It is generally accepted that the reaction is initiated by oxidation of a pyrrole molecule to form a radical cation. Two such species may then dimerize, with the subsequent loss of two protons (7). Dimeric or polymeric pyrrole oxidizes at a lower potential than pyrrole itself, so propagation of the polymer may occur by the analogous addition of pyrrole radical cations to polymeric radical cations. However, other evidence suggests that pyrrole radical cations are not involved after initiation (8), and propagation may occur by electrophilic attack of polymer radical cations on neutral monomers. There is scant evidence for the mechanism of chain termination, but a nucleophilic attack by water to convert a polypyrrole chain unit into a lactam ring has been proposed (9).

The extent of oxidation of polypyrrole film, reflected in the value of n in eq 1, can be easily altered by subjecting the film to a reducing potential. Reduction of the film requires a corresponding expulsion of dopant anions or an incorporation of cations, and both processes have been shown to occur when the film is reduced (1, 10). In its reduced form polypyrrole is a nonconductor; its conductivity increases to a limit with increasing oxidation level. Overoxidation causes degradation of the polymer.

The mechanism of conductivity of polypyrrole has been investigated extensively. The direct relationship between conductivity and temperature is typical of a semiconductor, although the conductivity of polypyrrole approaches that of a metal and is many times greater than that of a typical inorganic semiconductor. In reduced form the valence band and the conduction band of polypyrrole are widely separated. Oxi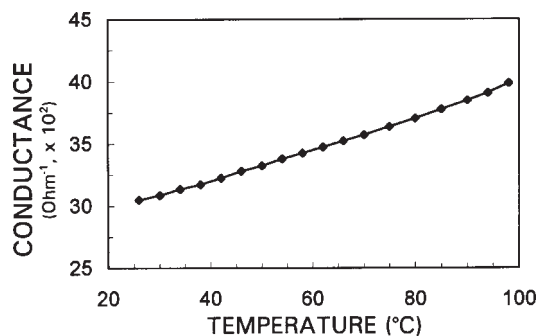dation produces a polypyrrole segment in a higher energy state, and the formation of many such segments results in a band of energies close enough to the valence band for a thermally controlled population distribution.

The removal of an electron during oxidation of polypyrrole generates a positive charge and an unpaired electron. The latter is displaced (polarized) some distance away from the positive charge, down a length of conjugated polymer chain. This polarized unit, called a "polaron", is the charge-carrying entity of lightly doped polypyrrole. At higher levels of oxidation a second electron is removed from the polaron, and the resultant doubly charged unit, called a "bipolaron", is the principal charge-carrying entity at optimum conductivity levels (1). The bipolaron has an even number of electrons, all paired, and hence conductivity in polypyrrole is often referred to as "spinless".

Its unique properties have led to some commercial applications of polypyrrole, despite the lack of a full understanding of its structure and conduction mechanisms. The polymer has been used in the manufacture of printed circuit boards, electrolytic capacitors, rechargeable batteries, and conductive coatings for textiles (11), and its commercial utilization is destined to expand in the future as further knowledge of the factors that affect its mechanical and electrical properties is discovered.

Notes

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