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STRUCTURAL EFFECTS IN POLYPYRROLE SYNTHESIS

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Abstract—Production of very thick polypyrrole films is an easy process, as the thickness can be controlled in a galvanostatic experiment by measuring the polymerization time. When using the p-toluene sulfonate anion, tough and flexible films with a high specific conductivity (70-90 $\Omega^{-1} \text{ cm}^{-1}$) are produced. These properties are the same for films, produced in both acetonitrile and aqueous solutions.

Both types of films contain a large amount of incorporated anion and solvent, even after drying in vacuo at room temperature.

In aqueous solutions a polymer film with tube-like bulges are formed, probably caused by a spiralled microstructure of the chain. In acetonitrile no such tubes are found.

INTRODUCTION

Since the first reports on the electrochemical synthesis of polypyrrole in 1979, an abundance of reports and papers have been published on the field of conducting polymers, and especially polypyrrole. Many articles were devoted to the experimental conditions during synthesis[1-12].

In the course of this worldwide investigation, it has become clear that the variation of the supporting electrolyte and solvent are of crucial importance as regards the properties of the resulting polymer. Water and many organic solvents (acetonitrile, alcohols, tetrahydrofuran etc) can be used as solvent. The solvent must be electrochemically inert during the oxidation of pyrrole (at 0.8-1.0 V vs see).

The choice of the supporting electrolyte, and especially the anion of the electrolyte, also has a great influence on the electrical and mechanical properties of the polypyrrole, since anions are incorporated in the polymer during its formation. For instance, the films with perchlorate as anion show a high conductivity and a low mechanical strength. However, when sulfonated phenyl derivatives are used, a high mechanical strength and a high conductivity are achieved[13]. Other anions (counter ions) give different combinations of mechanical strength and electrical conductivity[1-13].

During our investigations of the synthesis and application of polypyrrole we have found some remarkable structural effects in the formation of polypyrrole films, 100-200 $\mu$m in thickness, when using water as the solvent and tetraethylammonium p-toluene sulfonate as the electrolyte.

EXPERIMENTAL

The polypyrrole films were galvanostatically prepared on a Ni foil of 35 $\mu$m thickness and 20 cm$^2$ surface area. The polymerization solution consisted of 0.2 M pyrrole (Janssen Chimica), 0.2 M tetraethylammonium p-toluene sulfonate (Janssen Chimica) and doubly distilled water or acetonitrile (Janssen Chimica). The pyrrole was distilled before use and the p-toluene salts were dried for several hours in a vacuum desiccator; the acetonitrile was used as received. A constant current was supplied by a dc power supply (Delta Electronica E030-3). A variable resistor of 20 k$\Omega$ was placed in the current circuit. The experiments were carried out at room temperature in an undivided cell (50 x 50 x 60 mm) with Ni foil as the anode and a Ni or stainless steel plate as cathode (immersed area: 25 cm$^2$). The polypyrrole films were deposited on the anode at a constant current density varying from 2.5 to 10 mA cm$^{-2}$. It was found that the nature of the anode material had little effect on the properties of the polymer film formed. The polymer films, with a thickness of 100-200 $\mu$m, were separated from the Ni foil and dried in vacuum at room temperature.

RESULTS

Acetonitrile solutions

When acetonitrile was used as solvent, very tough films containing p-toluene sulfonate anions were produced. The films were flexible and showed high mechanical strength.

Electron micrographs of these films are shown in Fig. 1. No influence of the current density used to form the film could be detected from its appearance.

Aqueous solutions

Flexible, tough films of high mechanical strength were prepared in aqueous solution. However, the physical appearance of the film formed in aqueous

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solution differed totally from that formed in acetonitrile. On a macroscopic scale, tube-like structures were formed perpendicular to the surface of the film. A photograph is shown in Fig. 2 from which it follows that the tubes are hollow and have very thin walls. From a picture with a higher magnification, using the electron microscope, it has been found that the walls have a fine microscopic structure (Fig. 3A). The structure of the film surface is also different from that of films prepared in acetonitrile (Fig. 3B).

Fig. 1. Electron micrograph of a film, grown in acetonitrile with a current density of 6.25 mA cm$^{-1}$ for 50 min. Thickness 225 $\mu$m.

Fig. 2. Photograph of a polypyrrole film, grown in water with a current density of 4 mA cm$^{-1}$ for 10 min.
A typical composition of the films prepared from aqueous solution was: 57.00 % C, 4.60 % H, 8.83 % N and 29.57 % (S + O). This corresponds to the following molecular formula: \( \text{C}_4\text{H}_8\text{N} \text{C}_3\text{H}_7\text{SO}_3 \text{H}_2\text{O}_{0.40} \) with a composition of 56.99 % C, 4.62 % H, 8.78 % N and 29.61 % (S + O).

The appearance of the tubes depended on the current density used during formation of the polymer film, and on the time of polymerization. A higher current density led to more tubes per unit area and a longer formation time yielded longer tubes.

The conductivity of both types of films was
measured using the four-probe technique[14]. Samples of films, prepared in both water and acetonitrile, gave the same specific conductivity. A specific conductivity of 70–90 Ω⁻¹ cm⁻¹ was found for films with a thickness of 100–200 μm.

**DISCUSSION**

The excellent mechanical properties of polypyrrole films with incorporated p-toluene sulfonate or other benzene sulfonate derivatives is well known. Several papers have been published on this subject[13, 15]. No reason for this high mechanical strength has been given yet. Probably a strong interaction between the polypyrrole chain (the charged sections or bipolarons) and the p-toluene sulfonate anion is an approach to the answer. For both types of formation solution a high amount of the p-toluene sulfonate anion is incorporated in the film, the degree of insertion of anions, x = 0.69 for acetonitrile-based solutions and x = 0.51 for aqueous solutions. This indicates a polypyrrole chain with a higher charge per monomer than that obtained with "small" anions like ClO₄⁻ or BF₄⁻, for which x is about 0.25[2].

A much more "ordered" structure of the polypyrrole chains for p-toluene sulfonate is likely, as this molecule can serve as an "ordering" element. The polypyrrole chain will be more stretched out, permitting a higher charge per monomer (similar to the conjugation length in ordered and non-ordered polymer and polyelectrolyte solutions as mentioned by Odijk[16]). The use of small anions allows a more random configuration of the polymer chain.

The elemental analysis of both types of films shows that a residue of solvent remains in the film after drying in vacuum at room temperature. Small amounts of the solvent can be removed by heat treatment at 80–100°C and at reduced pressure (Wynne[15]).

The remarkable formation of tube-like structures in aqueous solution needs further consideration. As the tube-like structures may have a crystalline character, an investigation with X-ray techniques has been carried out. With the Debye–Scherrer camera a very weak diffraction pattern or none at all has been detected. Considering the small diameter and thin walls of the tubes, the crystallites can only be several nm thick and less than 1 μm wide. These numbers are below the detection limit for X-ray diffraction. It is possible that the tubes have a highly ordered structure.

Again, the reason for the forming the tubes is speculative, but because of the great interest in conducting polymers a tentative explanation for the formation of the tubes is given.

It is known that another conducting polymer, polythiophene, can be prepared in a highly fibrillar form[17, 18]. Garnier[18] assumed two different types of polymer chains, one type, the normal generally accepted structure, given in Fig. 4A and the other, a "twisted" structure, like that in Fig. 4B. The twisted structure leads to a spiralled polythiophene chain, forming a fibrillar macroscopic structure.

The same phenomenon can take place when pyrrole is involved. Fig. 5A shows the twisted structure for polypyrrole. The representations of the chain have been obtained with the help of the AMBER (Assisted Model Building with Energy Refinement)[19] and CHEMX programs at the Dutch CAOS/CAMM center. The spiralled structure (Fig. 5B) forms a hydrophobic environment for the hydrogen atoms, bonded to the nitrogen atoms of the polypyrrole chain. As the positive charges are situated on the backbone of the polypyrrole chain, this is turned outward to meet the water dipoles. These spiral fibrils cause a spiralled macroscopic structure and hence the form of the tubes.

When the p-toluene sulfonate anion is sandwiched between successive turns in the spiral, the ions give firmness to the structure by turning the sulfonate group outward to the aqueous environment and the phenyl group inward to the hydrophobic region.
There are several possible applications for these tube-like structures, for instance in membrane technology, turbulence promoters on electrodes and maybe even as microreactors.

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