

Structure, strength and electrical performance of conducting polypyrroles

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Polypyrrole films, typically 0.2 mm thick, were prepared by electrodeposition with *p* toluene sulphonate as dopant anions. Conductivities of up to 340 S cm^{-1} were found, comparing favourably with other cited examples. Conductivity along each sample was found to be much greater than across: such asymmetry may be exploitable. Electrodeposition temperatures (0°C) lead to higher conductivities than at 25°C . The structure was amorphous as indicated by X-ray diffraction, and the morphology was found to be nodular by using optical and scanning electron microscopy. Films were found to be quite strong and tough, although some reduction in mechanical performance was found after ageing in air. Fracture surfaces of tensile test pieces suggest a layered structure, with little evidence for viscous deformation being evident.

1. Introduction

Polypyrroles have been the subject of considerable interest over the last decade, due to their potential application in batteries [1-3], electrodes [4, 5], conducting composites [6, 7], stable solar cells [8, 9], and fuel cells and electrocatalysts [10]. Furthermore, they can be readily prepared by electrodeposition [8, 11] (anodic oxidation of pyrrole monomer solution) or by interfacial polymerization [12].

Polypyrrole films are amorphous and insoluble in organic solvents [5]. In the reduced state, polypyrrole is yellow-green, unstable and insulating but it rapidly transforms into the oxidized, stable state. Here it is black, stable and highly conductive. Polypyrrole has been shown by differential scanning calorimetry [13, 14] to be stable to 200°C , beyond which gradual but increasing weight loss occurs.

Surface morphology is typically described as being of "cauliflower" or nodular form, although it will vary depending upon the dopant anion [11], composition of the polymerization solution and applied current/potential used [15, 16]. Densities range from 1.37 to 1.58 g cm^{-3} depending upon the dopant anion [16]. The structure, as revealed by X-ray diffraction, is anisotropic [17].

Polypyrroles generally have conductivities between 10 and 100 S cm^{-1} but somewhat higher values can be achieved by modifications to the preparation procedure [18, 19]. It was recently shown [18] that when the polymerization temperature was lowered from 20 to -20°C , the conductivity increased from 97 to 287 S cm^{-1} .

The first polypyrrole samples were hard and relatively brittle (ϵ_b , the breaking strain, being 4 to 8%) [8]. Small amounts of water in the solvent can act as a plasticizer, with increased breaking strains of 8 to 18% [14] and 60% [20] being cited. In the latter case,

vacuum drying leads to modulus and tensile strength increasing by a third, but breaking strain fell to 15%.

Similarly, freshly prepared polypyrrole films containing 8% acetonitrile/water have an ϵ_b of almost 50% [14], but after drying this fell to 16%. Such plasticization is reversible. Low current densities and trace amounts ($\approx 1\%$) of water in the electrodeposition solution give higher elongations and ultimate tensile strength [15]. However, altering the polymerization temperature can also enhance mechanical properties, with increases in ϵ_b from 6 to 70-100% being reported as temperature decreases from 20 to -20°C [18].

In this work we describe polypyrrole films having superior electrical conductivity together with useful mechanical properties. Fracture properties have hitherto been seldom shown, and so some attempt to fill this gap is also made.

2. Experimental details

2.1. Polypyrrole synthesis

The method used is after that of Bloor *et al.* [15]. Propylene carbonate solvent (Merck-Schurhardt, synthesis grade, 220 g), 0.05 M tetraethyl ammonium *p* toluene sulphonate electrolyte and dopant anion (Alfa Products, 98%), 0.14 M pyrrole monomer (Fluka, "purum") and distilled water (1% vol/vol) were mixed until homogeneous. The mixture was transferred to a 500 ml cylindrical glass cell containing a $5 \times 2 \text{ cm}$ titanium working electrode and a carbon counter electrode (cathode). A saturated calomel electrode (SCE) was used as the reference. A voltage of 1.0 V versus the SCE was applied at the anode using a "B.W.D." dual power supply unit, model 24JA, at 0.3 to 1.0 mA cm^{-2} . The cell was kept either at 0 or 25°C , but no stirring or purge gases were used. After films of the desired thickness were formed the anode was removed, the

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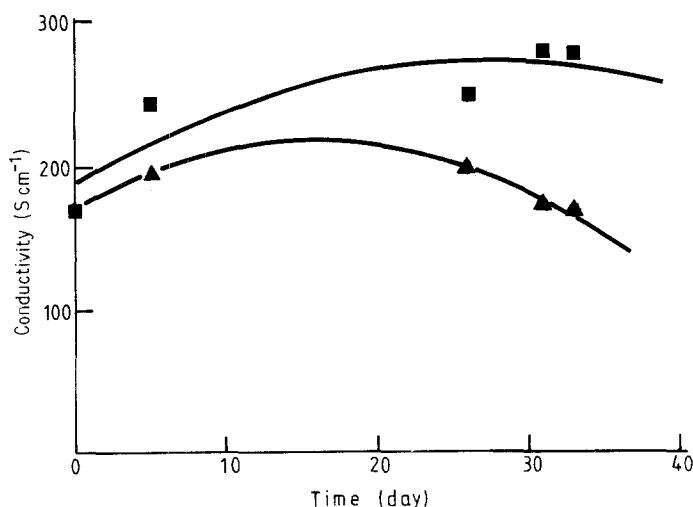


Figure 1 Variation of conductivity of polypyrrole *p* toluene sulphonate, prepared at 25°C, with ageing time, (▲) across the sample, (■) along the sample.

film was then removed using a scalpel and the electrode replaced. The time required for deposition of a 0.2 mm thick film was about 24 h.

2.2. Microscopy

Uncoated samples were examined using either a Jeol JSM-2 or a Cambridge Stereoscan S4-10 instrument. Optical micrographs of fracture surfaces were obtained using a Wild M420 microscope.

2.3. Electrical conductivity

Conductivity was measured using a four-probe technique [21]. A constant known current was applied to a 2 cm × 2 cm sample of constant thickness by connected probes. The potential drop is obtained using a multimeter. The current is then increased to another known value and the potential again measured. From a series of these measurements (typically ten were undertaken) a regression value of resistance and hence conductivity is obtained.

2.4. Tensile properties

Parallel-sided strips of polypyrrole approximately 3 to 4 mm wide and 5 cm long were tested in an Instron 1115 Universal Testing Machine. An intergrip distance of 2 cm and a cross-head speed of 0.5 cm min⁻¹ were employed. Although some samples were epoxy resin bonded to aluminium supports, those ≥ 0.2 mm thick could be legitimately tested in normal self-

retracting grips. No localized drawing down was observed and fracture was often away from the grip faces.

2.5. Thermal analysis

Thermal transitions were measured using a Du Pont Series 99 thermal analyser with 910 differential scanning calorimeter module. About 10 mg was heated from 30 to 360°C at 20°C min⁻¹ in a nitrogen atmosphere. Samples were crimped in aluminium pans and glass beads were used as a reference.

Thermal stability and determination of the volatile content were measured by heating 10 mg of the sample in the platinum boat of a Du Pont series 951 thermogravimetric analyser. The temperature was raised from 30 to 930°C at 20°C min⁻¹ and a nitrogen atmosphere was employed throughout.

2.6. X-ray analysis

A Rigaku "D-Max Geigerflux" unit was employed. The copper X-ray tube was operated at 35 kV and 35 mA.

3. Results

The properties and performance of polypyrroles will be described where polymerization temperatures of 0 and 25°C were used. Other synthesis conditions were maintained constant.

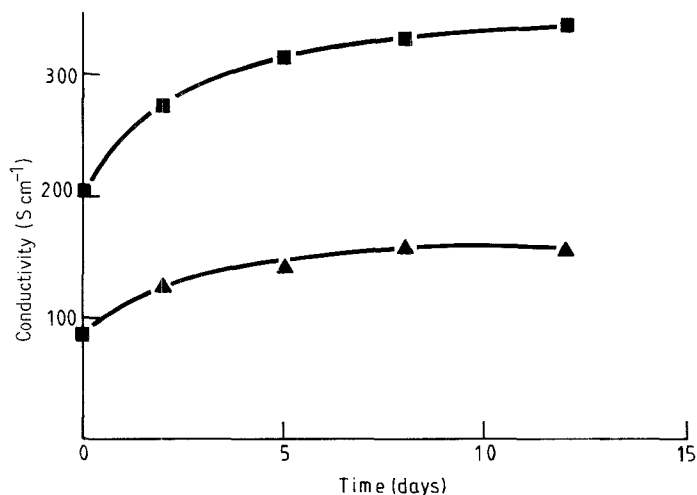


Figure 2 Variation of conductivity of polypyrrole *p* toluene sulphonate, prepared at 0°C with ageing time, (▲) across the sample, (■) along the sample.

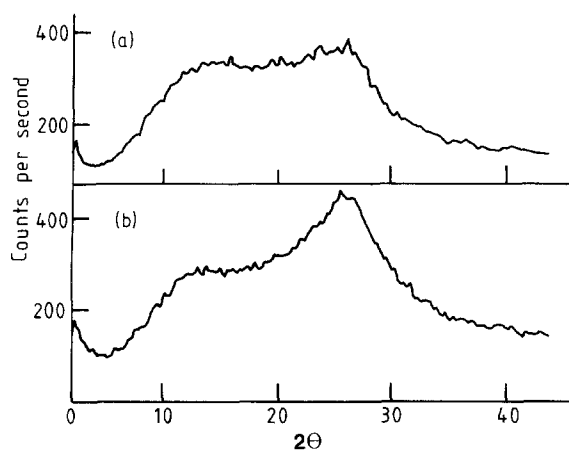


Figure 3 (a) wide-angle X-ray pattern of polypyrrole *p* toluene sulphonate. (b) Same film rotated through 90°.

3.1. Conductivity

Although all samples were quite conductive, ranging from 60 to over 300 Siemen cm^{-1} , three factors exerted considerable influence, these being polymerization temperature, sample ageing time and orientation of the film. Polypyrrole made at 25°C shows an initial conductivity of about 200 S cm^{-1} , this modestly increasing over the first 10 to 20 days ageing in air (Fig. 1). The improvement subsequently diminishes. Conductivity measured “along” the sample (i.e. in the longitudinal direction of the electrode) was somewhat higher than across the sample (transverse direction).

The polypyrrole prepared at 0°C also shows an increase in conductivity after ageing for 10 days in air. However, greater dichotomy is found in the directional influence upon conductivity, with the transverse direction being about three times less conductive than the longitudinal direction (Fig. 2). Furthermore, the maximum conductivity measured was over 330 S cm^{-1} , higher than that achieved at 25°C, and comparable with the highest values reported in the literature.

One possible cause of the observed anisotropic effect

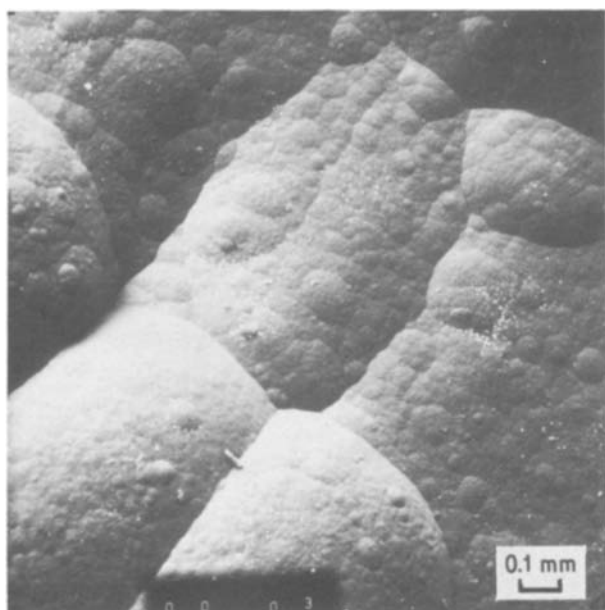


Figure 4 Nodular structure of thin polypyrrole *p* toluene sulphonate film surface.

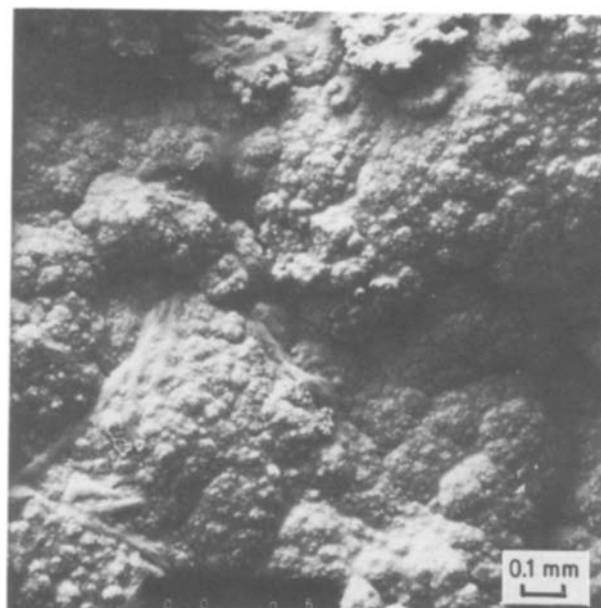


Figure 5 “Cauliflower” morphology of a thick (≈ 0.2 mm) rough polypyrrole *p* toluene sulphonate film surface.

was that the titanium electrodes might have had an oriented surface texture. However, in separate experiments where electrodes with surfaces deliberately scoured along and across the longitudinal direction, almost identical conductivity data were obtained. We believe that preferential alignment of dopant anions may contribute to the anisotropy observed. In addition, some anisotropy in the doped polymer structure was revealed by XRD. When the same sample was mounted in the X-ray beam in two positions, the second being normal to the first, a change in diffraction pattern, as shown in Fig. 3, was obtained.

3.2. Morphology

As expected, thick film grown over many hours showed a nodular morphology. During the first few hours thin films were macroscopically smooth, but SEM reveals the existence of microdomains typically from less than 50 μm to about 500 μm diameter. As polymerization continues, these domains become more pronounced as illustrated in Fig. 4. Thick films can be classified as “smooth” where little asperity is detectable, or rough, where the surface feels abrasive. In the latter case, nodules are very obvious (Fig. 5) and the morphology conforms to the “cauliflower” topology frequently alluded to in the literature. Little evidence can be found for anisotropy which is suggested from the conductivity and X-ray results given above.

TABLE I Tensile properties of polypyrrole toluene sulphonate prepared at 0°C

Sample condition	σ_b^* (MPa)	ϵ_b (%)	E (GPa)
As-received (tested within 45 h of synthesis)	43	26	2.7
After prolonged desiccation	36	3	1.0

* σ_b = breaking stress.

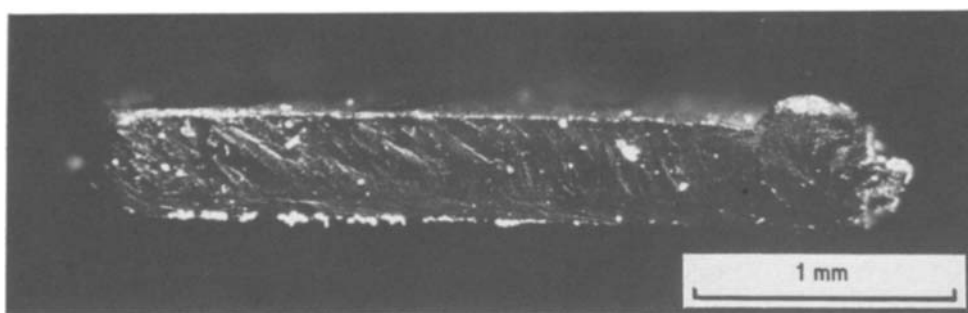


Figure 6 Optical micrograph of the fracture surface.

3.3. Mechanical properties

Samples were strained in the longitudinal direction, this allowing the longest specimens to be used. The data given in Table I represent the mean values for ten tests, and correspond to polypyrrole prepared at 0°C. Individual unaged samples showed strains up to 40% with no evidence of necking and with load continually increasing prior to fracture. Moisture and solvent (propylene carbonate) appear to act as plasticizers; their loss leads to substantial embrittlement.

Fracture surfaces of tough polypyrrole *p* toluene sulphonate were examined by optical and scanning electron microscopy. No evidence for local viscous deformation can be seen (Fig. 6). A lower edge about 100 μm thick can be distinguished from the rest of the fracture surface which has oblique striations extending to the upper surface.

The transition from bottom (relatively featureless) zone to upper striated zone can be also seen by scanning electron microscopy (Fig. 7), although more intensive examination at higher magnifications is hampered by specimen damage, attributable to loss of volatile components (Fig. 8).

The fracture surfaces indicate some textural anisotropy which may potentially explain directional electrical performance. However, this needs to be much more thoroughly investigated.

3.4. Thermal analysis

It can be seen that freshly produced films have high conductivity and good toughness but that whilst conductivity continues to improve with ageing, mechanical performance deteriorates. Moisture loss is reflected

by an endotherm at 105°C in the DSC (Fig. 9), but the exotherm located at 235°C needs to be attributed to either a crystallization process (polymer or dopant) or some chemical change. It is unlikely to be due to loss of propylene carbonate (b.p. 242°C) as this would appear as an endotherm. Above 300°C thermal degradation is slight, with little perturbation in the trace being detected.

TGA traces of as-received and aged samples showed little difference with low temperature (i.e. ≤ 200°C) weight losses being from 7 to 11%, whilst total weight loss at 800°C ranged from 38 to 44%. No correlation between extremes in these ranges and ageing history could be made. A typical trace is shown as Fig. 10. The thermal stability of these samples can be seen to be unusually high compared with most commodity and engineering polymers, where dramatic temperature losses due to depolymerization are common.

4. Discussion

The polymer films described in this work have conductivities which are of the same order as those described by others (e.g. example [18, 19]) and mechanical performance approaches that described by Bloor *et al.* [15]. Preliminary findings with films prepared under our conditions but using acetonitrile as solvent suggest conductivities of the order of 800 S cm⁻¹, and further advances in this area will be the subject of a future communication. However, the principal finding reported here is the variation in conductivity with sample orientation, a characteristic which has previously been seldom mentioned. This may be a potentially useful property, which we are presently

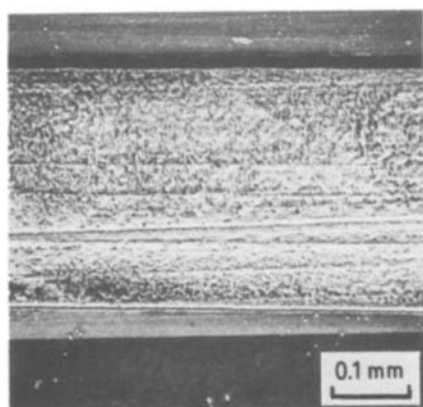


Figure 7 Same fracture surface showing two morphologies (SEM).

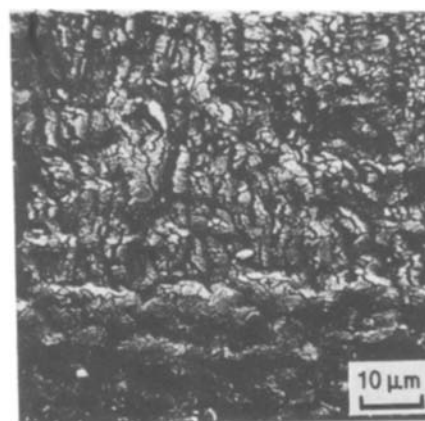


Figure 8 Fracture surface showing beam damage (SEM).

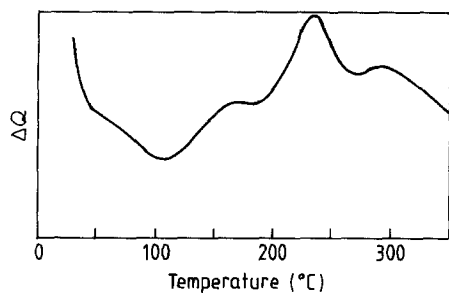


Figure 9 Differential scanning calorimetry trace of polypyrrole toluene sulphonate.

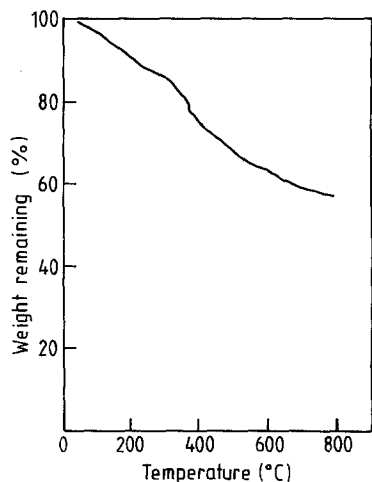


Figure 10 Thermogravimetric analysis weight loss trace for polypyrrole *p* toluene sulphonate.

seeking to reinforce by modifications to our preparative methods.

Acknowledgements

The provision of photographic assistance by S. Preece and C. W. Yao and line drawings by B. Kortvelyesy is acknowledged.

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Received 26 May

and accepted 22 September 1987