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Enhanced thermal properties and morphology of ion-exchanged polypyrrole films

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The thermal stability of electrochemically prepared polypyrrole (PPy) films with *p*-toluenesulfonate (*p*TS) or perchlorate (ClO_4^-) counterion (PPy/*p*TS and PPy/ClO_4^-) is improved by simple treatment with aqueous sulfuric acid, sodium sulfate or sodium bisulfate. The degree of stabilization achieved depends on the solution, temperature and duration of treatment. Although the mechanism for improved stability is not yet clear, it is apparent that the level of ion exchange and the original polymer microstructure are important. A model for the conductivity decay as a function of thickness has been proposed. The early stages of ion exchange are not symmetrical, and diffusion is facilitated at the electrode side of the film. Furthermore, X-ray diffraction shows no evidence of morphological change after treatment of PPy/*p*TS (43 μm), but in PPy/*p*TS (12 μm) and PPy/ClO_4^- (41 μm) films an additional peak is indicative of more ordered structure following treatment. The glass transition temperature, T_g, of PPy/*p*TS and PPy/ClO_4^- films obtained by modulated differential scanning calorimetry is approximately 155°C.

(Keywords: polypyrrole films; ion exchange; thermal properties)

INTRODUCTION

The stability of electrical properties of electro-active polymers is an essential criterion, if these materials are to be considered for use in electronic devices and other applications. Encapsulation of conducting polymers in epoxy was an early countermeasure to oxidative degradation leading to the loss of conductivity. This method, however, precludes the many applications where encapsulation is undesirable, and in the last decade the need for unprotected conducting polymers in oxidative and high-temperature environments has attracted considerable attention to the degradation mechanisms and conductivity decay in a variety of conducting polymers, such as polyacetylene, polyaniline, polypyrrole (PPy) and polythiophene. These research activities have been summarized in an excellent review by Billingham and Calvert[1].

From an application point of view, PPy has been considered as one of the best candidate materials because of its greater electrical stability at ambient temperature compared to polyacetylene. At elevated temperatures (60–150°C), however, the conductivity rapidly declines[2,3]. In an attempt to understand the degradation mechanisms of PPy films, the effect of dopants[2,3], film thickness[4] and anisotropy through the film[5] on the loss of conductivity during thermal ageing have been studied in detail. Investigation of oxidative degradation has recently been extended to PPy powders and PPy-coated textiles[6]. Because of the difficulty in characterizing these materials, these studies are mainly phenomenological by nature. The link between chemical and physical changes of the aged polymer–dopant systems and loss of conductivity has not been established. Nevertheless, there has been some empirical success in improving the thermal stability by ion exchange of the counterion dopant. Münstedt[7] achieved enhanced thermal stability of PPy films by treating them with dilute acid and/or base. He related the improved stability of the treated film, which retained up to 70% of its initial conductivity after 100 days at 140°C, to a decrease in oxygen and water vapour permeability.

This work will focus on the thermal degradation and the stabilization of electrical properties of electrochemical PPy films doped with *p*-toluenesulfonate (*p*TS) and perchlorate (ClO_4^-) counterions after treatment with sulfuric acid, sodium bisulfate or sodium sulfate solutions at various temperatures. The effect of film thickness (PPy/*p*TS films) and dopants on the conductivity decay at elevated temperature and the improved stability of the treated films will be discussed.

EXPERIMENTAL

PPy films were prepared by electrodeposition in distilled water. Pyrrole monomer was distilled under nitrogen. The polymerization solution contained freshly distilled

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Table 1 Conditions of treatment for polypyrrole films

Treatment No.	Solution	Temperature/Duration
1	H_2SO_4 (0.5 M)	100°C/1 h
2	H_2SO_4 (0.5 M)	20°C/1 h
3	H_2SO_4 (0.5 M)	50°C/1 h
4	$NaHSO_4$ (0.5 M)	100°C/1 h
5	Na_2SO_4 (0.5 M)	100°C/1 h
6	$NaHSO_4$ (1 M)	20°C/4 days
7	Na_2SO_4 (1 M)	20°C/4 days

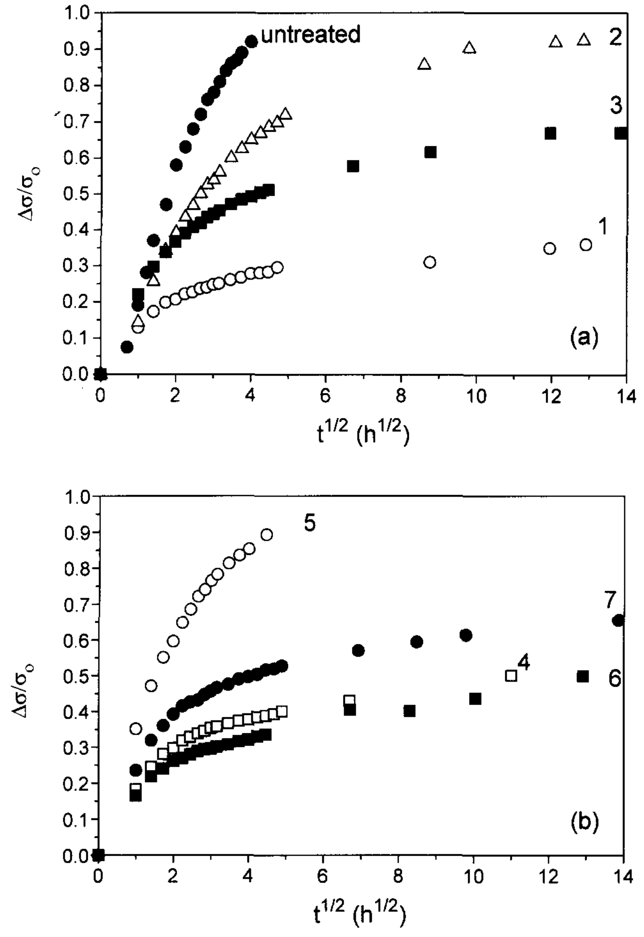

Figure 1 Conductivity decay $\Delta\sigma/\sigma_0$ as a function of time $t^{1/2}$ of PPy/*p*TS film (12 μm) at the ageing temperature of 150°C. The number denotes the treatment number (*Table 1*)

pyrrole (0.1 M) and dopant (0.1 M). Sodium *p*-toluenesulfonate (>98% purity, Merck) and tetraethylammonium perchlorate (>99% purity, Fluka) were used as dopants without further purification.

Electrodeposition was performed at a constant current of 2.8 mA cm^{-2} using horizontal stainless-steel electrodes under a nitrogen blanket. The deposition time was varied to obtain films of different thickness for PPy/*p*TS, and was 2 h for PPy/ClO_4^-. The film was removed from the electrode and washed with a mixture of water and acetonitrile (1:1 by volume) to remove excess dopant. The treatment conditions for ion exchange are listed in *Table 1*.

Thermal ageing was performed in dry air at 150°C in a laboratory oven. Conductivity was determined *in situ* by the four-probe method at a constant current of 0.5 mA. Morphological change was observed by wide-angle X-ray diffraction and the composition by scanning electron microscopy with energy-dispersive X-ray spectroscopy.

RESULTS AND DISCUSSION

Stabilization of PPy films

Figures 1 and *2* show the effect of the various treatments with dilute sulfuric acid and its sodium salts on the conductivity decay of two thicknesses of the PPy/*p*TS film. The decay of conductivity is measured as the normalized value $\Delta\sigma/\sigma_0$ (where $\Delta\sigma$ is the difference between the initial conductivity σ_0 and the conductivity σ after thermal ageing time t). It is noted that, when the rate of decay is relatively high, both the untreated and treated samples show that conductivity decay is proportional to $t^{1/2}$, but this proportionality rapidly disappears in stabilized films. For example, both thin and thick films treated with sulfuric acid at 100°C (treatment No. 1) exhibit very high thermal stability, where only a small initial drop in conductivity was observed before stable conductivity was maintained for long periods. A common feature of the treated films is that during thermal ageing the conductivity decreases to a constant value, i.e. a residual conductivity, the rate and extent of decay depending on the treatment conditions. Thick films show better stabilization as the rate of decay is slower and the

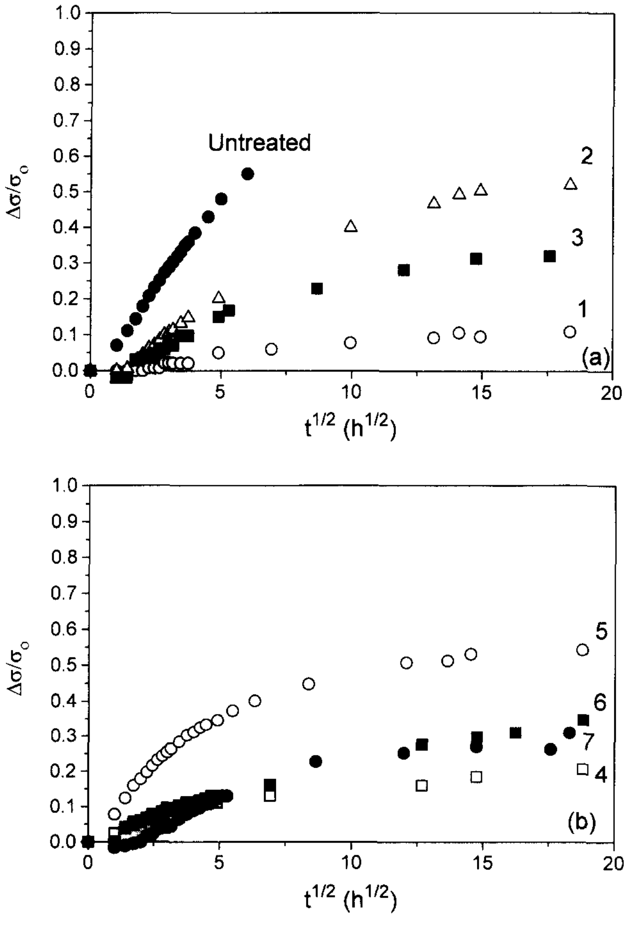

Figure 2 Conductivity decay $\Delta\sigma/\sigma_0$ as a function of time $t^{1/2}$ of PPy/*p*TS film (43 μm) at the ageing temperature of 150°C. The number denotes the treatment number (*Table 1*)

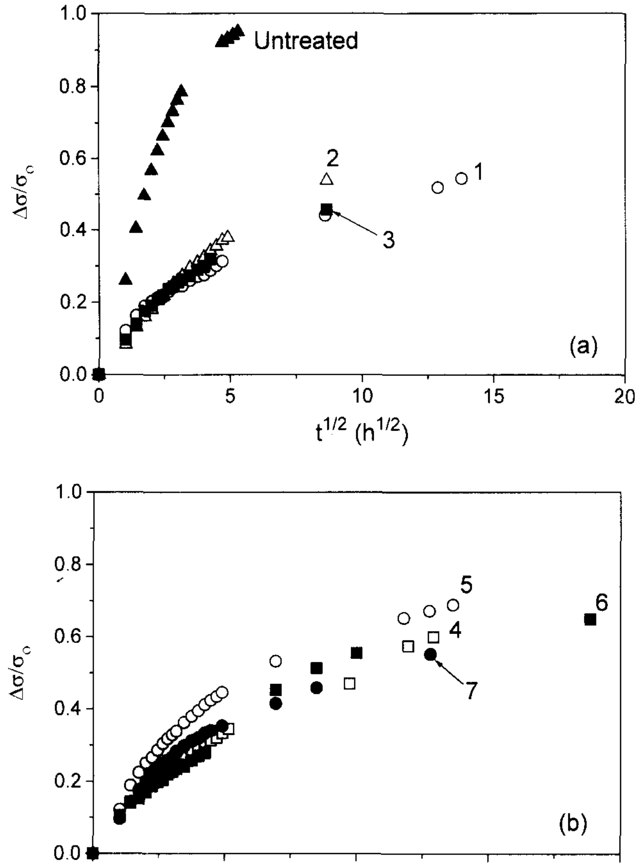

Figure 3 Conductivity decay $\Delta\sigma/\sigma_0$ as a function of time $t^{1/2}$ of PPy/ClO_4^- film (41 μm) at the ageing temperature of 150°C. The number denotes the treatment number (*Table 1*)

loss of conductivity smaller. In the case of untreated film it has been shown that the effect of thickness on the rate of conductivity decay is consistent with diffusion-controlled kinetics[3,8].

Increasing the temperature of the acid treatment (treatment Nos. 1, 2, 3) should accelerate the exchange of the counterion and it is found that, after the same treatment time, films treated at high temperature decay more slowly and have higher residual conductivity. On the other hand, when the dopant was dodecyl sulfate (DDS) the PPy/DDS films were not stabilized by the acid treatment[3], and it has been shown by solid-state n.m.r.[9] that exchange of the long-chain DDS ion is difficult.

It may be expected that, since HSO_4^- is a weak acid ($K_a = 1.2 \times 10^{-2}$), it is the ion exchange with HSO_4^- that confers thermal stability in the H_2SO_4 treatment. Using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/e.d.s.) and mass balance, Münstedt[7] confirmed that HSO_4^- rather than SO_4^{2-} replaces the original dopant during acid treatment. While the treatment with $NaHSO_4$ or Na_2SO_4 reduces the conductivity of PPy/*p*TS (to 0.8–0.9 times the initial conductivity), treatment with acid increases the conductivity (by 1.2–1.3 times) and this is attributed to protonation[10]—as the conductivity of polyaniline is controlled by the degree of protonation[11]. *Figures 1* and *2* show that PPy/*p*TS films treated with $NaHSO_4$ (treatment No. 4) and H_2SO_4 (treatment No. 1) under the same exchange conditions exhibit different rates of conductivity decay, but in both cases the counterion has been replaced by HSO_4^-. Although the concentration of HSO_4^- will be increased by protonation during acid treatment of the film, there is a possibility that (a) protonation may affect the stabilization of the conductivity independently of the exchange between *p*TS and HSO_4^- and/or (b) the ion-exchange kinetics are dependent on the associated cation (H^+ or Na^+).

The enhanced thermal stability of films treated with Na_2SO_4 suggests that *p*TS was replaced by SO_4^{2-}, and is consistent with the lower exchange rate of SO_4^{2-} compared to monovalent HSO_4^- previously reported[12]. If stabilization is related to the degree of exchange of dopant, then treatment No. 7 provided a more complete exchange of SO_4^{2-} for *p*TS than treatment No. 5 in both thin and thick films. In contrast, whereas it is not possible to distinguish between the decay of thin films after the $NaHSO_4$ treatments No. 4 and No. 6, the thick films show short and hot No. 4 to be more effective than long and cold No. 6. Despite this, these four treatments achieved similar stabilization of the thicker film. The effect of the valency of the dopant on stabilization of PPy film against thermal decay is not fully understood and clearly further investigation is needed. However, it could be argued that there is less exchange of divalent SO_4^{2-} but that it is more effective.

Figure 3 shows the decay of conductivity at 150°C of PPy/ClO_4^- films before and after treatment with dilute sulfuric acid or sulfate solutions. The decay curves of the treated PPy/ClO_4^- films are different from those of PPy/*p*TS films in two respects. First, in contrast to the PPy/*p*TS films (*Figures 1* and *2*), they are much less dependent on the treatment; and, second, the curve plateau observed in the treated PPy/*p*TS films is not always achievable for PPy/ClO_4^- films. This indirectly highlights a basic difference between these films; the stability of the dopant. While *p*TS is relatively stable at high temperature, ClO_4^- can disproportionate:

$$ClO_4^- \rightarrow Cl^- + 2O_2$$

In order to determine the effect of the decomposition of ClO_4^-, a PPy/ClO_4^- film was aged at 150°C in a nitrogen atmosphere for 48 h. The 40% reduction of conductivity observed for the PPy/ClO_4^- films can be contrasted with the relative stability (<5% decay) of PPy/*p*TS or PPy/DDS films under the same ageing conditions[3]. It is believed that the counterion can oxidize the polymer backbone and disrupt the conjugation, thus lowering the conductivity. The loss of conductivity in air will be the additive result of atmospheric and counterion oxidation, and if these processes are independent the difference between conductivity decay during ageing in nitrogen and air can be attributed to atmospheric oxidation. This difference is shown in *Figure 4* (curve c). Since treatment No. 1 removes all the ClO_4^- (see below), this treated film should only be subject to atmospheric oxidation; however, its stability (*Figure 4*, curve d) is consistently greater than this prediction (*Figure 4*, curve c). This reflects the expected reduction of oxygen diffusivity in the treated film.

In considering the stability of treated ClO_4^- films, it is important to know the contribution, if any, of the remnant ClO_4^- to the oxidation. E.d.s. determination of Cl and S can show a profile of the progressive replacement

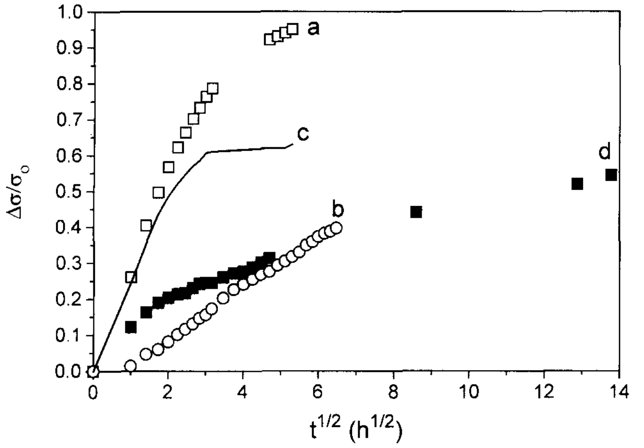

Figure 4 Conductivity decay $\Delta\sigma/\sigma_0$ as a function of time $t^{1/2}$ of PPy/ClO_4^- film (41 μm) at the ageing temperature of 150°C: (a) untreated sample in air; (b) untreated sample in dry nitrogen atmosphere; (c) difference between curves (a) and (b); and (d) treatment No. 1 sample in air

of ClO_4^- by HSO_4^- or SO_4^{2-} during treatment. *Figure 5* shows that the replacement is rapid and largely complete for most treatments other than sodium sulfate solutions. Yamaura *et al.*[12] have shown that the exchange rate of counterions in PPy depends on the affinity of the anion for the polymer backbone, and is in the order $HSO_4^- < p\text{TS} < ClO_4^-$, so that the last is readily replaced. When the replacement is incomplete, the conductivity decay will be complex since, while the skin will be partially stabilized against oxygen diffusion, the core is still at risk of self-oxidation because of the high level of ClO_4^- remaining. This would explain why the plateau of thermal stabilization was not observed in PPy/ClO_4^- films. The relative stability of the various treated films can be qualitatively explained by these considerations. For example, the substantial level of unexchanged Cl observed at the core of the films after treatments No. 2 and No. 5 (*Figure 5*) would explain the more rapid decay of these samples compared to those from treatments Nos. 1, 3, 4, 6 and 7 (*Figure 3*).

It has been shown that after treatment No. 1 HSO_4^- completely replaced the ClO_4^- in PPy/ClO_4^- films (*Figure 5*) and the *p*TS in PPy/*p*TS films (shown by n.m.r.[9]). In each case the exchange is accompanied by a small increase in conductivity, attributed to protonation of the polypyrrole. Pei and Qian[10] have recently reported that protonation has little effect on the electronic structure of the PPy chain, and Yamaura *et al.*[12] have reported that anion replacement in PPy/PF_6^- with a variety of counterions preserved the conductivity of the parent film, indicating insignificant perturbation of the electronic structure or changes in chemical and higher-order structures. It seems unlikely that the most vigorous of these treatments (No. 1) has a significant effect on the as-grown microstructure of the parent film. Treatment No. 1 of PPy/*p*TS (43 μm) and PPy/ClO_4^- (41 μm) gave films that had very different decay rates and residual conductivity (*Figures 2* and *3*), and this suggests that the initial microstructure, unchanged by counterion exchange, has a critical role in the thermal degradation and self-stabilization of electrical conductivity of these materials.

A model for conductivity decay

When the conductivity of PPy film of thickness l and initial conductivity σ_0 decays as a result of thermo-oxidative degradation, it is envisaged that the diffusion of oxygen into the film results in an inhomogeneous film and a progressive change from oxidized outer layers to an unaffected core region. If it is assumed that, after some degradation time t, the oxidized layers (both sides) have a combined thickness l_1 and an average conductivity σ_1, which is independent of the film thickness, then the measured conductivity σ based on a parallel circuit is given by:

$$\sigma l = \sigma_1 l_1 + (l - l_1)\sigma_0 \qquad (1a)$$

or

$$\sigma/\sigma_0 = (\sigma_1/\sigma_0 - 1)(l_1/l) + 1 \qquad (l > l_1) \qquad (1b)$$

Since σ_1 and l_1 are constants at a given time t, the plot of σ/σ_0 vs. l^{-1} is linear. If the film thickness l is smaller than l_1, i.e. if there is no virgin core, then σ_1 will not be independent of film thickness, and equation (1) will not be obeyed. Under some conditions it may be possible to make a further assumption that the oxidation is the same on both sides of the film. It has been shown[5], by blocking access of air to one face and measuring the conductivity decay, that at 150°C oxidation is the same at both faces of an unstabilized film. However, the appearances of the two sides of the film are different (smooth at the electrode face, cauliflower-like on the growth face), ion exchange is not always symmetrical (*Figure 5*) and the 'oxidation symmetry' is temperature-dependent, so this assumption cannot be adopted for stabilized film without testing.

Figures 6 and *7* show the σ/σ_0 vs. l^{-1} for the untreated and treated samples, respectively, at various times during the first 36 h of ageing at 150°C. For the untreated samples (*Figure 6*), the plots are linear for thick samples but not for thin samples, and the deviation from linearity occurs at greater sample thickness for longer ageing times. The film thickness at the deviation from linearity represents a limit of film thickness l_1 at the particular time below which there is no virgin unoxidized core and σ/σ_0 does not obey equation (1). In contrast to the untreated film, there appears to be no clear-cut end to linearity for the treated samples, and this could be best attributed to the presence of 'virgin' material in the core of the thinnest film even after 36 h and 90% loss of conductivity. This would imply a slow oxygen diffusion process leading to a thinner oxidized layer compared to the untreated samples. Extrapolation of the linear part of the plots in *Figures 6* and *7* gives an intercept value ($l^{-1} = 0$) of σ/σ_0 in the range 0.9–1.2. Considering the simplistic model and the inherent experimental uncertainty, this agreement with equation (1) is adequate. *Figure 8* plots l_1 determined for untreated film (*Figure 6*) against $t^{1/2}$. The initial linearity of this plot strongly suggests the diffusion control of oxidation previously reported[3,8].

The difficulty of characterizing PPy is a major obstacle in understanding the structure–property relationships and the thermo-oxidative mechanisms that lead to the loss of conductivity during thermal ageing. The present model of a layered structure might be useful in understanding the stabilization. It is thought that as the outer layers are oxidized the average conductivity of the affected region decreases from σ_0 to σ_1, and at the same

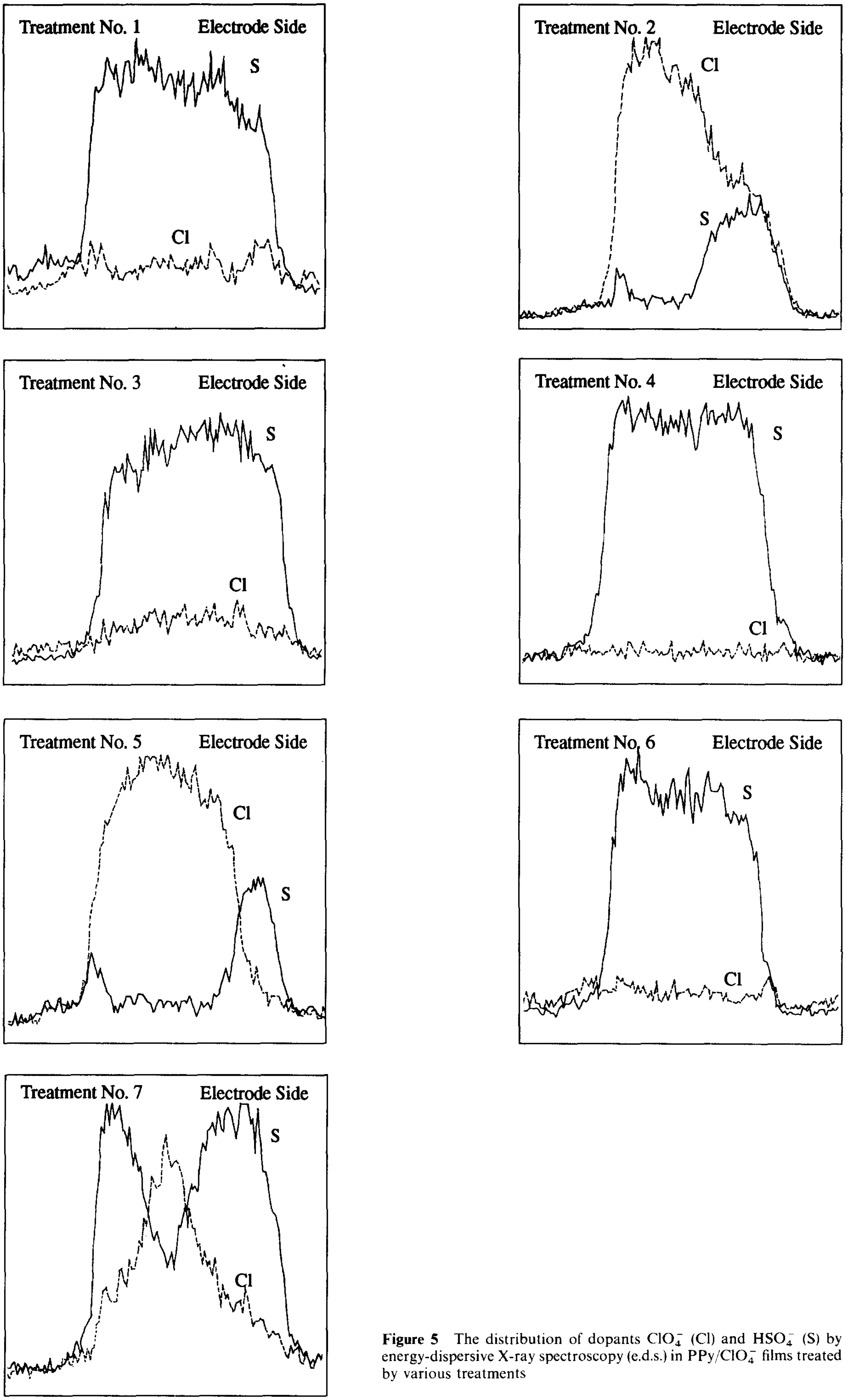

Figure 5 The distribution of dopants ClO_4^- (Cl) and HSO_4^- (S) by energy-dispersive X-ray spectroscopy (e.d.s.) in PPy/ClO_4^- films treated by various treatments

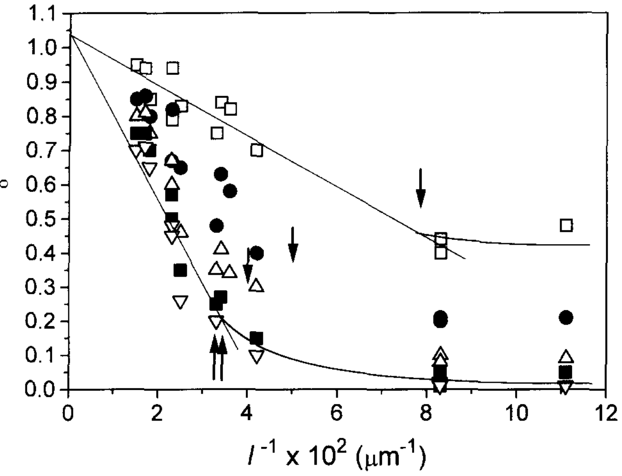

Figure 6 Relation between the normalized conductivity σ/σ_0 and the inverse value of film thickness l^{-1} of untreated PPy/*p*TS films. Ageing time *t*: (□) 4 h; (●) 9 h; (△) 16 h; (■) 25 h; and (▽) 36 h. The curves were shown for data at $t = 4$ and 36 h as an example and the linear part was obtained by linear regression. The arrows mark the thickness of the oxidized layers l_1 where deviation from linearity occurs

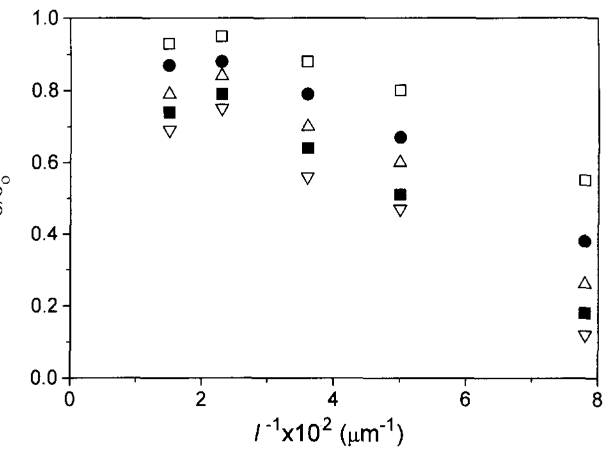

Figure 7 Relation between the normalized conductivity σ/σ_0 and the inverse value of film thickness l^{-1} of treated PPy/*p*TS films by treatment No. 1. Symbols as in *Figure 6*

time the oxygen permeability of the material is decreased and the rate of conductivity decay is reduced. Ultimately the stage is reached where the oxidized outer skin protects the pristine core from further oxidation. Münstedt[7] reported that after treatment the PPy films had better thermal stability and reduced permeability to oxygen and water vapour and we have observed self-stabilization (limited decay of conductivity) in thick PPy/*p*TS films ($\geqslant 40$ μm)[8].

It is suggested that as a result of ion exchange oxygen diffusion into the film is retarded and the affected zone more restricted, but the mechanisms of this stabilization are not immediately obvious. Purely physical explanations for reduced oxygen diffusion are unlikely; densification of the film during the exchange was considered but linear shrinkage was no more than 5% and scanning electron microscopy showed that the nodular surface was essentially unchanged.

Morphological modification of ion-exchanged PPy

Wide-angle X-ray diffraction experiments on treated films indicate that there is long-range order in the polymer backbone, and that it can be modified during treatment of the film. *Figure 9* shows a high-angle peak at $2\theta = 27°$ for PPy/*p*TS and 22° for PPy/ClO$_4^-$. In the thick PPy/*p*TS film this peak is broadened by another peak at 20°. Warren *et al.*[13] have reported the same two peaks in PPy/*p*TS; the broad scattering reflects the disordered nature of PPy and the high-angle peaks indicate order in the polymer backbone. After treating

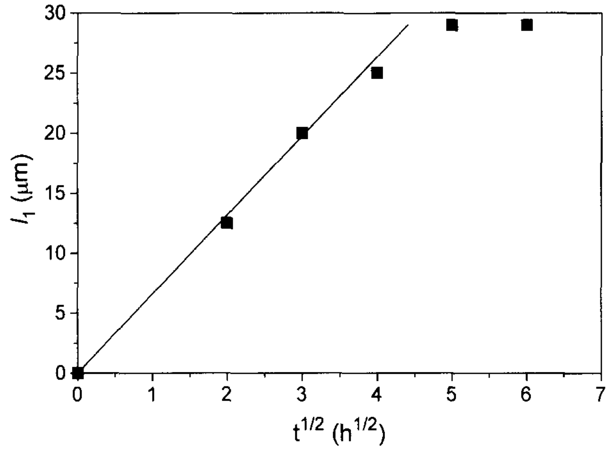

Figure 8 The thickness of the oxidized layers l_1 obtained from *Figure 6* as a function of time $t^{1/2}$

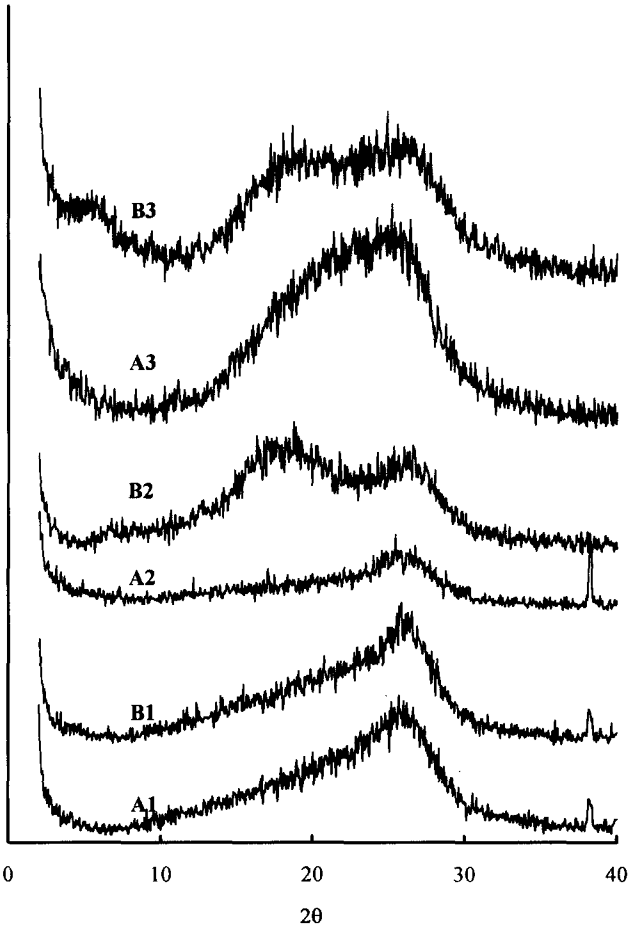

Figure 9 Typical X-ray diffraction patterns: 1, thick PPy/*p*TS film (43 μm); 2, thin PPy/*p*TS film (12 μm); and 3, PPy/ClO$_4^-$ film (41 μm); A, untreated; and B, treated by No. 5 (*Table 1*)

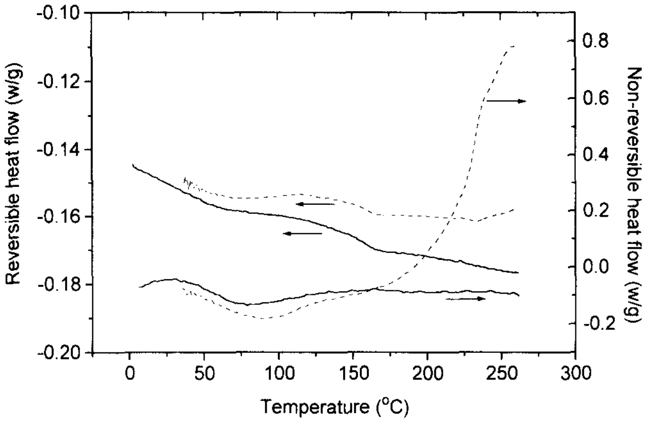

Figure 10 M.d.s.c. curves of PPy films showing the reversible and non-reversible components of the total heat flow. The T_g is observed in the reversible curves of both films while the self-oxidation of the PPy/ClO_4^- film is shown as a non-reversible effect. PPy/*p*TS (———) and PPy/ClO_4^- (– – –)

thin PPy/*p*TS and PPy/ClO_4^- with dilute sulfuric acid, a new peak appears at $2\theta = 17°$ while the pattern is unchanged for the thick PPy/*p*TS film. The new long-range order cannot be explained by solvent-induced crystallization, since no change occurs on prolonged soaking or boiling in water, and it must be mediated by ion exchange. Recently, Min *et al.*[14] introduced the concept of 'secondary doping' where the primarily doped polyaniline was exposed to *m*-cresol to induce crystallization and thus enhance the conductivity by a factor of three orders of magnitude. The new long-range order induced by an electrolyte solution in the PPy films may present a different phenomenon where a substantial increase in conductivity was not detected.

The absence of morphological change in the PPy/*p*TS thicker film is not immediately explicable, since PPy/ClO_4^- of the same thickness does show the new peak. It has been suggested that a high degree of order and orientation in the initial material deposited on the electrode surface ($<0.9\,\mu$m) is soon lost in the increasingly amorphous bulk material[15], but this is on a much smaller scale than the difference between the present thick and thin (12–43 μm) films. Increasing the electrolyte pH[16] and variations in voltage[17] noticed during the electrodeposition with a constant current can affect the chemical compositions and microstructures of the films with the growth time. The appearance of the new peak at $2\theta = 17°$ after treatment of PPy/ClO_4^- and thin PPy/*p*TS films may indirectly reflect the effect of changing synthesis conditions during the electrodeposition for the thin and thick PPy/*p*TS films and of dopants for the thick PPy/*p*TS and PPy/ClO_4^- films on the microstructures and morphology of the polymer. These effects merit further study.

The asymmetric ion exchange with sulfuric acid or its sodium salts shown at the initial stage by the sulfur e.d.s. profile (*Figure 5*) of the PPy/ClO_4^- films indicates chemical and/or structural differences between the 'electrode' surface and growth surface of the PPy/ClO_4^- film. The growth side of the film exhibits a lower exchange rate than the electrode side, and the different exchange kinetics of the two sides of the film may indicate (a) a low concentration of dopant on the growth side, or (b) different diffusivities or ionic affinities as a result of microstructural differences between the two sides. Assumption (a) is unwarranted as the cross-sectional Cl concentration of untreated samples shows a uniform distribution by e.d.s., whereas assumption (b) is consistent with the concept of a gradual change in microstructure as the thickness increases[15].

Thermal analysis

Previously it has been reported that the thermal analysis of PPy films is beset by ambiguity. Multiple reactions and thermo-oxidative crosslinking have obscured a putative T_g in both t.m.a. and d.s.c. investigations[8], and while isothermal d.s.c. studies using gas switching showed that the oxidation was detectable, it was neither quantifiable for ageing studies nor exclusively related to loss of conductivity[3]. No useful differences between treated and untreated films (either *p*TS or ClO_4^-) were detected using conventional t.m.a. or d.s.c. In isothermal d.s.c. the shape of the exotherm following the change of sweep gas from nitrogen to air may indicate kinetic and perhaps mechanistic differences between the various materials; in particular, while it was reported that for untreated material the rate of oxidation slowly decreased after an initial exothermic pulse[3], in several of the present materials the oxidation rate slowly increased after the initial pulse. Because of the small signal and procedural difficulties, no reliable quantitative measurements were obtained and, although there was some indication of reduced oxidation in stabilized materials, the disparity of timescale and temperature between isothermal d.s.c. and thermal ageing experiments was too great.

On the other hand a new technique, modulated differential scanning calorimetry (m.d.s.c.)[18,19], may offer some promise of characterizing these materials. In this technique the heat flow associated with irreversible change is uncoupled from that arising from reversible changes so that, for example, a glass transition can be seen separately from an endothermic dehydration or an exothermic reaction; and moreover, given proper experimental parameters, the ambiguities of baseline assignation are effectively reduced.

Preliminary experiments, like those in *Figure 10*, clearly show the dehydration of the PPy film, its glass transition (155°C) and, in the case of PPy/ClO_4^-, the high-temperature exothermic reaction. Initial indications are that ion exchange has little or no effect on the T_g of these films and would support the contention that the polymer backbone is unchanged. However, the experimental parameters have not been optimized, and we intend further work on the effect of film thickness, dopant, stabilization and ageing on the m.d.s.c. curves of PPy.

CONCLUSIONS

The results obtained from this study are basically phenomenological. The reactions relating to the loss of conductivity in thermal ageing, and the chemical processes underlying improvement of stability induced by ion exchange, using dilute sulfuric acid or its sodium salts, have not been identified. Nevertheless, useful information has been obtained. The experimental data of the conductivity decay are consistent with a multilayer model, in which the formation of a barrier to oxygen diffusion at the outer boundaries retards and ultimately arrests the advancing thermo-oxidative degradation. Despite the effectiveness of stabilizing electrical properties of PPy/*p*TS and PPy/ClO_4^- by ion exchange with H_2SO_4 or its sodium salts, the general applicability of the method to other PPy and dopant systems should not be assumed. This study has shown that improvement of thermal stability of PPy films is strongly dependent on the treatment conditions and properties of the exchanging electrolytes (valency of the guest anions, associated cations), which control the degree of ion exchange, and the inherent microstructures of the parent PPy networks.

The role of host anions in morphological modification observed in thin PPy/*p*TS and PPy/ClO_4^- films and the difference in exchange kinetics between the two film surfaces are not understood. These observations, however, confirm the anisotropic nature of the PPy film and suggest that the order of the nascent layers becomes less distinct with increasing thickness.

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