

Thermal stability of polyfuran/pechlorate doped films

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Abstract

Thermogravimetry, Fourier transform infrared spectroscopy and scanning electron microscopy were performed on polyfuran films to assess thermal stability. The influence of temperature on the structure and morphology of doped polyfuran conducting films was discussed. Thermal degradation began around 95°C, although aromaticity, structure and ordered nodular morphology in the growth face and the honeycomb appearance in the cross-section were partially conserved until about 210°C.

Introduction

Polyfuran (PFu) belongs to polymers with an extended π -electron system. They can be transformed by partial oxidation or reduction processes into conducting materials or materials with conductivity very sensitive to some gas action, humidity or temperature. It is possible to produce electrochemically these polymers as homogeneous films with controlled thickness, through a process in which the simultaneous insertion of counterions takes place.

Recently, stable polyfuran films doped with sodium perchlorate (PFu/ClO₄) have been obtained by anodic coupling of furan (Fu) (1-3), in spite of the reported difficulties for their synthesis (4,5). PFu/ClO₄ films exhibit a reproducible electrochemical behaviour (2) and higher aromaticity (6) than the previously synthesized by others authors (4,5,7). The morphology of PFu/ClO₄ films reveals an ordered structure never before obtained in other conducting polymers (8,9).

To the best of our knowledge there are no references concerning thermal degradation

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of PFu doped films, other than a brief note by Tourillon and Garnier (10) reporting that PFu films, like other conducting polymers, resisted temperatures of about 300-400°C. However, this assumption was not supported by any experimental evidence.

The aim of this work was to study the thermal stability of electrochemically synthesized PFu/ClO₄ films by thermogravimetry (TG), and the influence of temperature on the polymer structure by Fourier transformed infrared spectroscopy (FTIR) and morphology by scanning electron microscopy (SEM). It is known that many of the applications of conducting polymers such as batteries, sensors, membranes and electrochemical devices are based on their electroactive switching properties. In this sense, exposure to elevated temperatures is quite possible and changes in their structure could take place (chain defects, chain branching/crosslinking, etc)

Experimental

PFu/ClO₄ films were potentiostatically generated onto platinum electrodes at electropolymerization overpotential, η_p , 2.8 V (SCE) and time, t_p , 1800 s in acetonitrile (MeCN, Carlo Erba, RPE quality) dried over 3Å molecular sieves. The electrolyte, sodium perchlorate (NaClO₄, Aldrich Chemie, 99%) and monomer, furan (Fu, Aldrich Chemie, 99%), concentrations were 0.1 M. A potentiostat/galvanostat PAR 273A controlled by a PAR Model 270/250 Research Electrochemistry Software 4.00 was used. Experimental details concerning PFu/ClO₄ film formation have been already described (2,3,6). Slight variations in experimental conditions yielded films essentially exhibiting the same thermal behaviour.

Thermal stability was studied on finely divided (randomly orientated) samples of about 2 mg taken from room temperature vacuum dried PFu/ClO₄ films. It was carried out by using a previously calibrated thermogravimetric system Perkin-Elmer TGS2/TADS3700 at 10°C·min⁻¹ of heating rate from 30 to 500°C, under nitrogen purge of 5cm³·min⁻¹. In order to analyze the structural and morphological changes associated to thermal degradation, proper samples of PFu/ClO₄ films were prepared by TG at 210, 300 and 500°C.

Differential scanning calorimetry by a Perkin-Elmer DSC-2C/TADS 3700 with a liquid nitrogen unit (B012-8743) was employed at subambient temperature in the range from -73 to 50°C to detect the presence of residual solvents.

PFu/ClO₄ infrared spectra were obtained at room temperature in the region 4000-400 cm⁻¹ using a Fourier transform interferometer NICOLET 60SX equipped with a DTGS detector. All the spectra were recorded at 1 cm⁻¹ resolution and 32 scans were averaged to

improve the signal/noise ratio. The instrument was purged with dry air. Infrared spectra were registered from pressed discs of each PFu/ClO₄ sample mixed with KBr powder. The background (air + KBr) spectrum was removed by subtracting from film spectra.

The morphological study of PFu/ClO₄ films, before and after thermal treatment, was developed by scanning electron microscopy with a JEOL model JSM 6400 electron microscope at 20 kV. Samples were coated by sputtering with a thin gold film to avoid charge buildups because of their low conductivity. More details of the sample preparation were described elsewhere (8,9).

Results and discussion

Thermal stability study of PFu/ClO₄ films suggested no detectable weight loss before 95°C, but decomposition was nearly complete at 500°C, the weight loss being around 75% (Figure 1). Thermal degradation, TG curve, could be roughly divided in three weight loss overlapping steps.

The first step with ~27% loss (95 - 210°C) was attributed to perchlorate thermal decomposition and its elimination from the polymer matrix. It was clearly observable by the first peak of the corresponding DTG smoothed trace of Figure 1 with maximum lost effect at ~200°C, onset temperature at 164°C (130°C for the free chemical). Residual strongly absorbed acetonitrile and water still retained in the vacuum dried films were detected by low

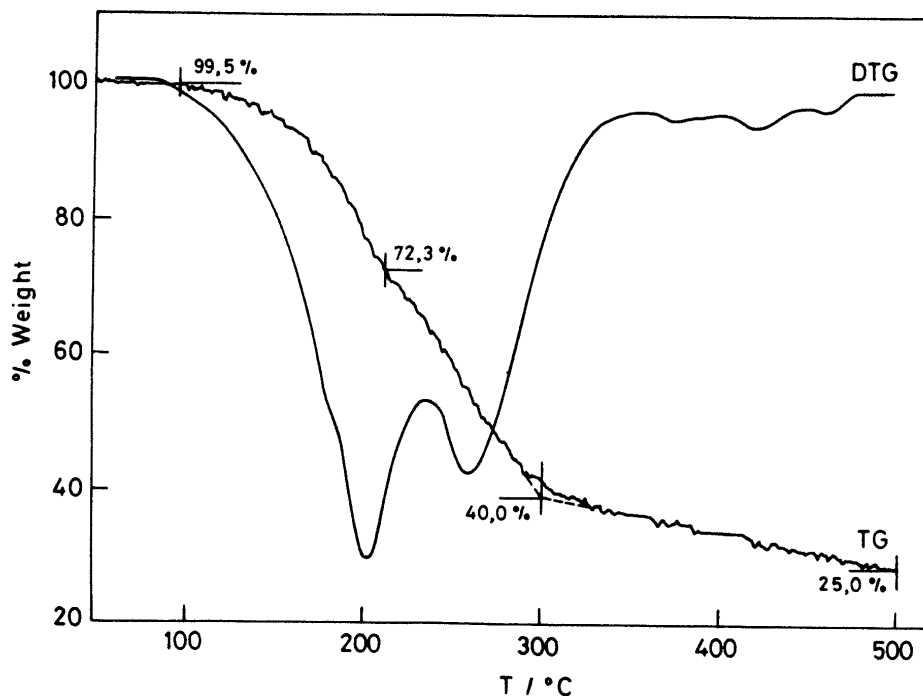


Figure 1. TG and DTG curves of PFu/ClO₄ films from 30 to 500°C.

temperature DSC as very small and broad endothermal effects centered at around -43°C (acetonitrile melting point, -46°C) and 0°C , respectively. The presence of these substances could be favoured by the porous films morphology previously described as in polypyrrole films (11). Residual absorbed water has been also observed in conducting vacuum dried polyaniline films, PANi, obtained either chemically or electrochemically (12-15). The next weight loss step ($210\text{-}300^{\circ}\text{C}$, TG curve) more clearly shown by the DTG second peak (maximum loss effect at $\sim 260^{\circ}\text{C}$), could be essentially assigned to the beginning of thermal breakdown of the polymer backbone as it happens in other conducting polymers (14,16). Loss (from deeper sites than before) and degradation of dopant persisted. From 300°C upwards an asymptotic tendency in the weight loss was detected corresponding to the entire polymer degradation.

Figure 2 shows FTIR spectra of PFu/ ClO_4 films before (Figure 2a) and after TG treatment (Figures 2b and 2c). The spectrum of PFu/ ClO_4 films before TG treatment was similar to the one obtained previously in other synthesis conditions (6). The film spectrum changed when the temperature increased up to 210°C (Figure 2b). The main difference with respect to Figure 2a was a decrease in the relative intensity of the absorption bands centered

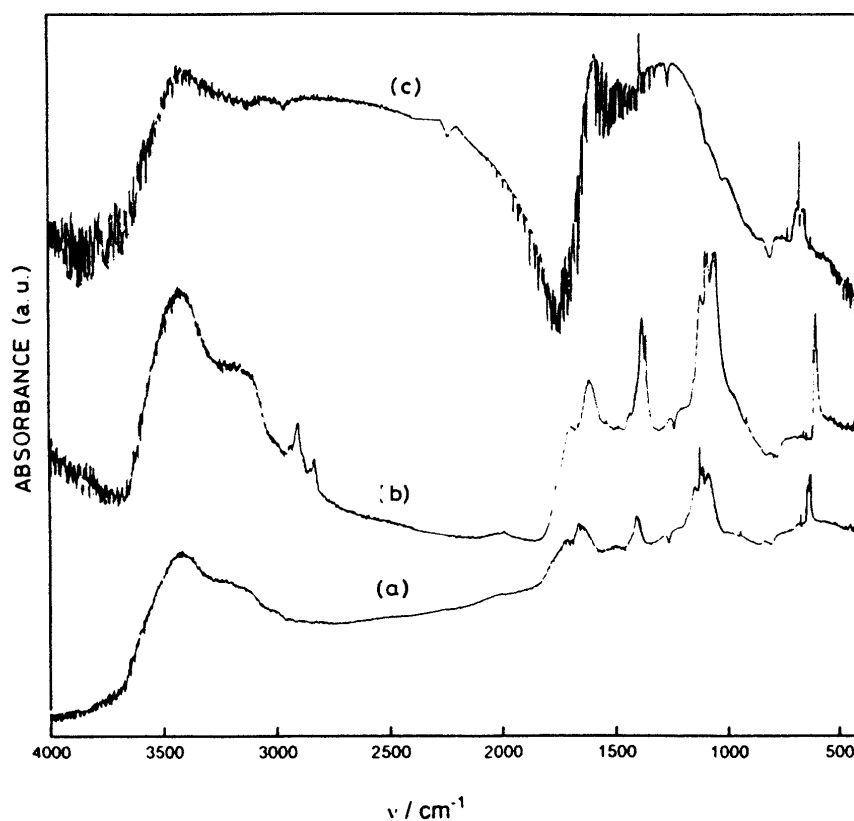


Figure 2. FTIR spectra of PFu/ ClO_4 films before (a) and after TG treatment (b) at 210°C and (c) 500°C .

around 1100 cm^{-1} , Cl-O stretching vibration, and 600 cm^{-1} , OClO symmetric bending vibration, which indicated lower presence of ClO_4^- in coherence with TG results. This fact was confirmed by energy dispersive X-Ray microanalysis carried out on these samples. It was also observed a better detection of aliphatic CH stretching vibration (2824 and 2858 cm^{-1}) and the appearance of a band corresponding to CH bending vibration (1398 cm^{-1}) which seemed to indicate the presence of CH_3 groups. These facts could imply the ring rupture and subsequent reduction which was also confirmed by the decrease in the relative intensity of the OH and C=O stretching vibration bands (3300 and 1720 cm^{-1} , respectively). In spite of it, the presence of the bands around 3145 and 1400 cm^{-1} , which correspond to the CH aromatic stretching vibration and a combination band due to C=C aromatic ring stretching and ring deformation vibrations, respectively, in the IR spectra showed that the aromatic character was still maintained. When temperature was increased up to 300°C , the corresponding spectrum (similar to the previous one) showed a progressive loss of ClO_4^- (nearly complete) and of aromaticity. An arrangement of the side chain could have taken place as in PANi (16). Samples treated at 500°C exhibited an spectrum (Figure 2c) with dramatic changes with respect to the previous ones. Film decomposition was nearly complete, the IR spectra showing ClO_4^- groups absence and high absorption of carbon species.

Scanning electron micrographs before any thermal treatment revealed different surface topographies on each side of the PFu/ ClO_4 . The growth face (Figure 3a) was matt and quite regular, exhibiting small nodules clustered together which form an extended ordered structure. The back face of the films was bright, more homogeneous and smoother than the other, nodules not being discernible. The cross-section of the films showed a porous texture composed by interlinked nodular layers with some cavities between them (9). It is interesting to remark the high level of order observed not only in the surface exposed to the solution.

SEM micrograph of PFu/ ClO_4 films after TG treatment at 210°C is shown in Figure 3b. Heat decomposition in the films growth face was quite visible, but the ordered structure was still maintained in some parts (arrows) in coherence with FTIR results. Also, some crystal structures appeared on the surface (asterisks). The cubic crystals were also observed on the smooth back face of the PFu/ ClO_4 films but in much larger amount. They were initially assigned to NaCl derived from ClO_4^- thermal decomposition and residual Na^+ remaining in the film from its electrogeneration process. An anodic polarization will induce p-doping process accompanied by the insertion of anions (X) from the electrolytic solution ($\text{P} + y\text{X}^- \rightleftharpoons \text{P}(\text{X})_y + ye^-$), the residual cation could be resting in the solution media or absorbed on the surface.

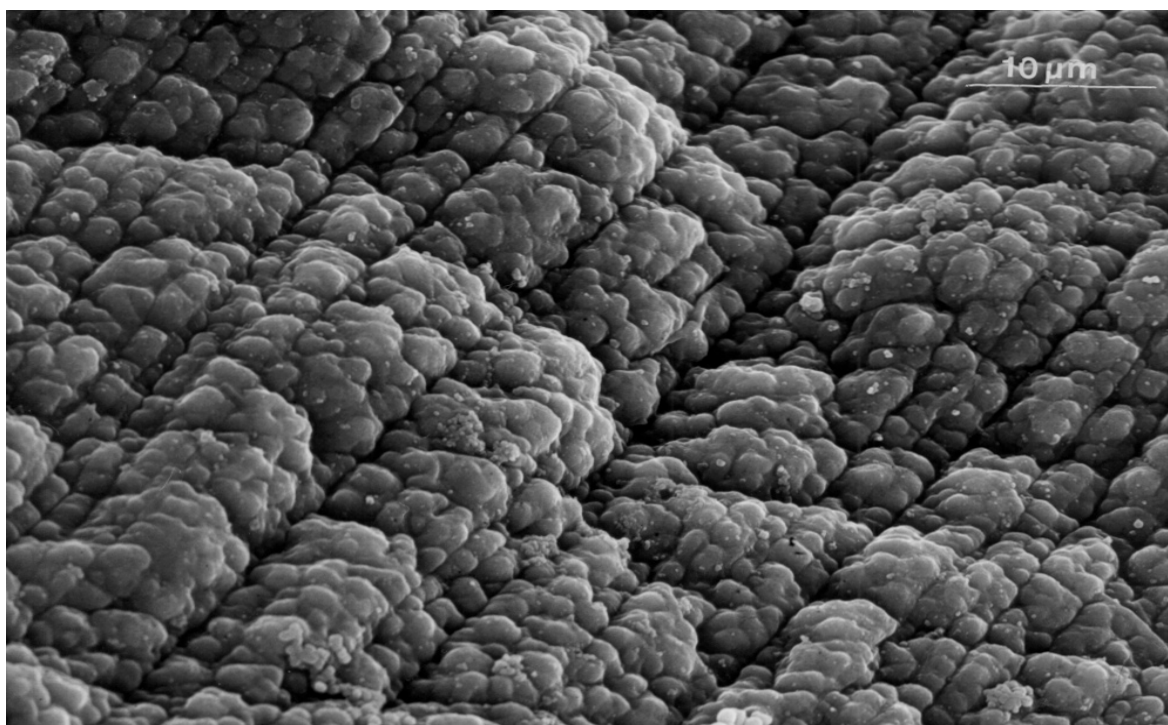


Figure 3a

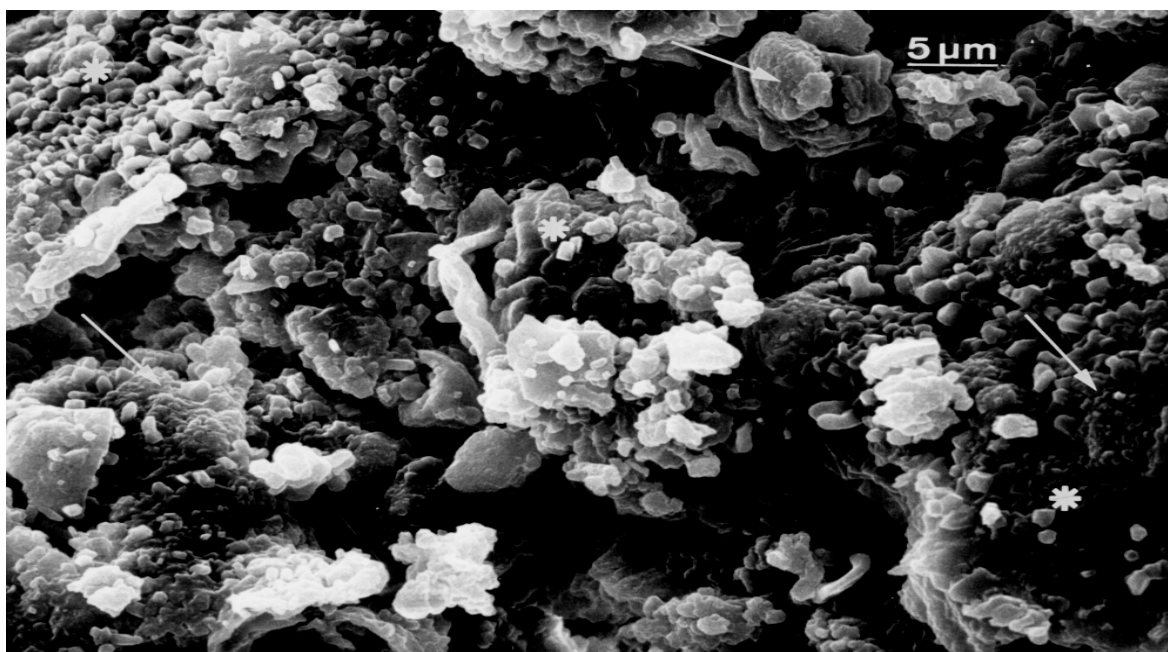


Figure 3b

Figure 3. Scanning electron micrographs of the growth face PFu/ClO₄ films a) without any thermal treatment, and after thermal treatment; b) until 210°C (→) ordered structure and (*) NaCl crystals; c) until 500°C (→) ordered structure.

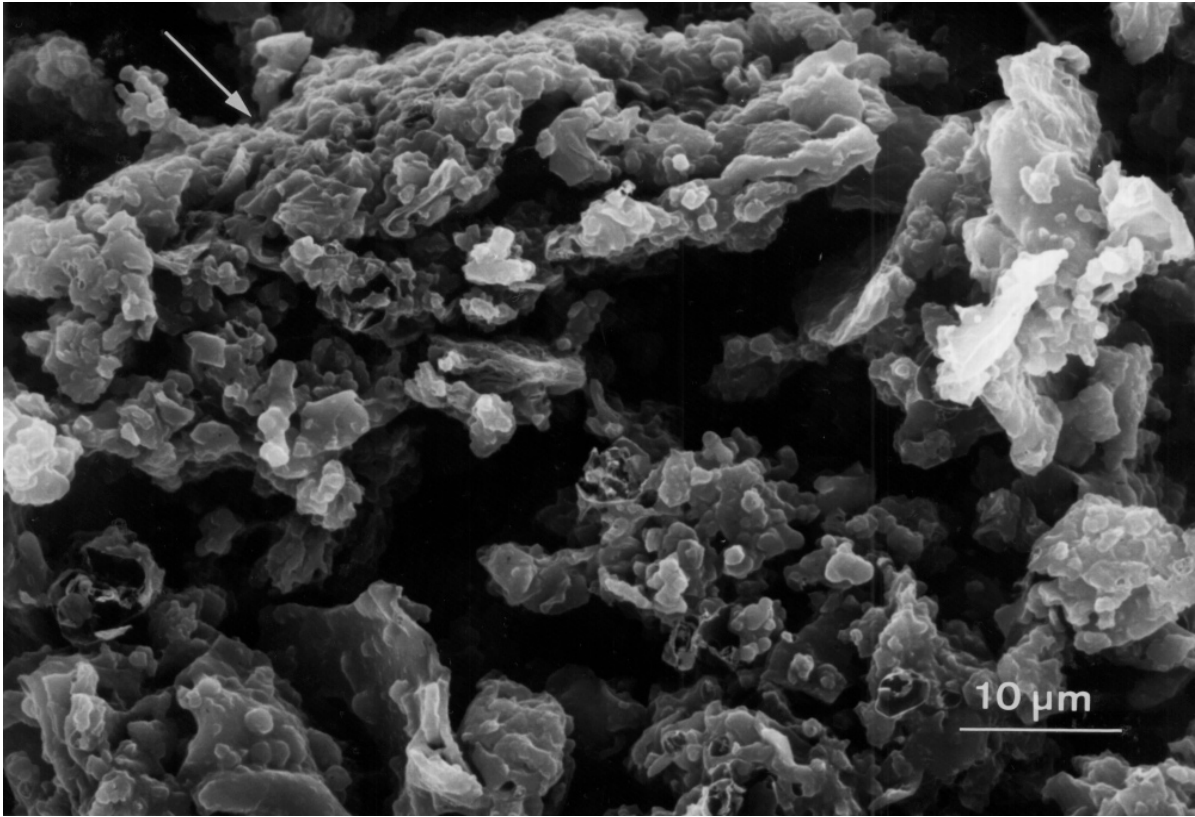


Figure 3c

Figure 3c shows a SEM micrograph of the growth face of the sample treated at 500°C. It exhibited some holes, indicative of material losses caused by the polymeric matrix destruction. However, original morphology could still be seen locally in the micrograph (arrows). The back face was cracked and a granular appearance with practically no crystals on the surface was detected. NaCl was almost completely sublimated, the respective microanalysis by EDX-Ray indicating a strong loss of chlorine in agreement with the corresponding FTIR spectrum. The characteristic laminar structure of the film cross-section was completely lost after this treatment. An intermediate morphological situation, but much closer to that of 500°C than to 210°C, was observed in the films treated up to 300°C (not shown).

In conclusion, black, adherent and homogeneous PFu/ClO₄ films, potentiostatically synthesized, were thermally stable up to 95°C. From this temperature upwards a progressive destruction of structure and morphology was ascertained. It consisted in a continuous loss of the dopant, aromaticity and ordered appearance (~200°C), followed by the polymer backbone rupture (~300°C) and final carbonization (~500°C). These results are in opposition to the claim that these kinds of films are thermally stable up to 300-400°C.

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