Chemical structure of polypyrrole: X-ray photoelectron spectroscopy of polypyrrole with 5-yliden-3-pyrrolin-2-one end groups

Josep M. Ribó[*] and Amadou Dicko
Department of Organic Chemistry, Faculty of Chemistry, University of Barcelona, Diagonal 647, E-08028 Barcelona, Catalunya, Spain

and Josep M. Tura
Laboratory of Physical Analysis Techniques, CSIC-IEC, E-08028 Barcelona, Catalunya, Spain

and D. Bloor[†]
Department of Physics, University of London, Mile End Road, London E1 4NS, UK

(*Received 30 October 1989; accepted 15 March 1990*)

After oxygen uptake, the two faces (electrode and solution faces) of an electrochemically obtained polypyrrole film show different elemental and chemical composition (X-ray photoelectron spectroscopy analysis). In contrast, polypyrrole with 3,4-dimethyl-3-pyrrolin-2-one end groups, obtained under the same experimental conditions, shows only slight differences in oxygen content and chemical composition. The presence of peroxide groups is proposed to account for the high oxygen contents in polypyrrole films.

(Keywords: chemical structure; polypyrrole; X-ray photoelectron spectroscopy; end groups)

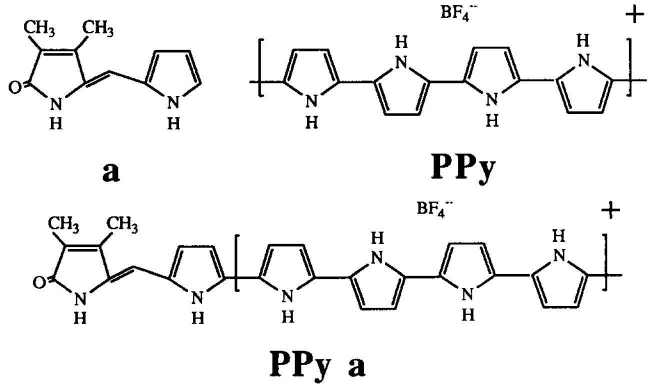
INTRODUCTION

We have previously[1] published the first results obtained by electrochemical copolymerization of pyrrole with dipyrrin-1(10*H*)-ones. The dipyrrinones acting as end groups of the polymer give, by copolymerization with pyrrole, films similar to that obtained with pyrrole alone. Elemental analysis of these films suggests that the dipyrrinone is incorporated as end groups in the film at a ratio of one end group to 20–30 pyrrole rings. Although this results in some soluble products, the bulk of the polymer is obtained as an insoluble film due to the presence of crosslinks. This is in contrast with end-group inclusion using 3,4-dimethylpyrrole and 2,3,4-trimethylpyrrole, where soluble oligomeric products are obtained[2]. These films show high oxygen contents, which is characteristic of oxidized polypyrrole (PPy) films after air contact[3–7].

X-ray photoelectron spectroscopy (X.p.s.) has previously been applied to the analysis of polypyrrolic materials[6–12], but these results do not allow the chemical structure differences between the real and the ideal structures of polypyrrole to be inferred. However, they show the differences, originating from the different growth and handling procedures, between the polypyrrole materials. The results presented here, using X.p.s., show the differences between polymer films obtained from pyrrole alone (PPy) and those obtained from copolymerization (PPy a) of pyrrole and 2,3-dimethyl dipyrrin-1(10*H*)-one (a) at a molar ratio of 10:1; see *Scheme 1*.

EXPERIMENTAL

PPy and PPy a were obtained as already reported[1,13], using tetraethylammonium tetrafluoroborate (TEAT) as supporting electrolyte in anhydrous propylene carbonate. Air was rigorously excluded during the electrochemical procedure, but not in the washing and drying work-up procedure. Films 0.20 mm thick were obtained with conductivities $>20\ \Omega^{-1}\ \mathrm{cm}^{-1}$; their properties are described elsewhere[1]. The samples were mounted on a stub with colloidal silver and analysed with 48 h of preparation. The air contact time was the same for all the PPy and PPy a films analysed. The X.p.s. spectra were obtained by means of a VG Scientific Escalab MK II. $\mathrm{AlK}_{\alpha 1,2}$ radiation was used as exciting source. All the experiments were carried out at a pressure $<10^{-9}$ torr (10^{-4} Pa) both in the chamber of the analyser and in the region of the source. The X-ray source was operated at



Scheme 1

---

[*] To whom correspondence should be addressed

[†] Present address: Applied Physics Group, School of Engineering and Applied Science, University of Durham, Durham DH1 3LE, UK

0032-3861/91/040728-05

a constant power of 240 W (12 kV, 20 mA). A constant voltage of 20 V was applied through the hemispheres of the electron analyser which operated in the CAE (constant analyser energy) mode attaining a value of f.w.h.m. of 1.4 eV for the Au $4f_{7/2}$ transition. The spectra were calibrated by assuming a C 1s peak due to residual hydrocarbon to have a binding energy of 285 eV. Charging effects were not observed. High resolution scans were recorded on individual peaks using a pass energy of 25 eV. Samples were positioned at a 40° take off angle.

Elemental surface stoichiometries were obtained from the relative peak intensities (from general scans) and peak surfaces (from high resolution individual scans) of the 1s levels and were corrected with the appropriate atomic sensitivity factors[14]: errors of 15% compared with the real surface elemental stoichiometry may be expected. However, because the samples were analysed under the same experimental conditions, i.e. identical analytical and work-up procedure after film preparation, the error in relative stoichiometries between films must be of a lower order of magnitude.

RESULTS AND DISCUSSION

Table 1 shows peak intensity and peak surface relative

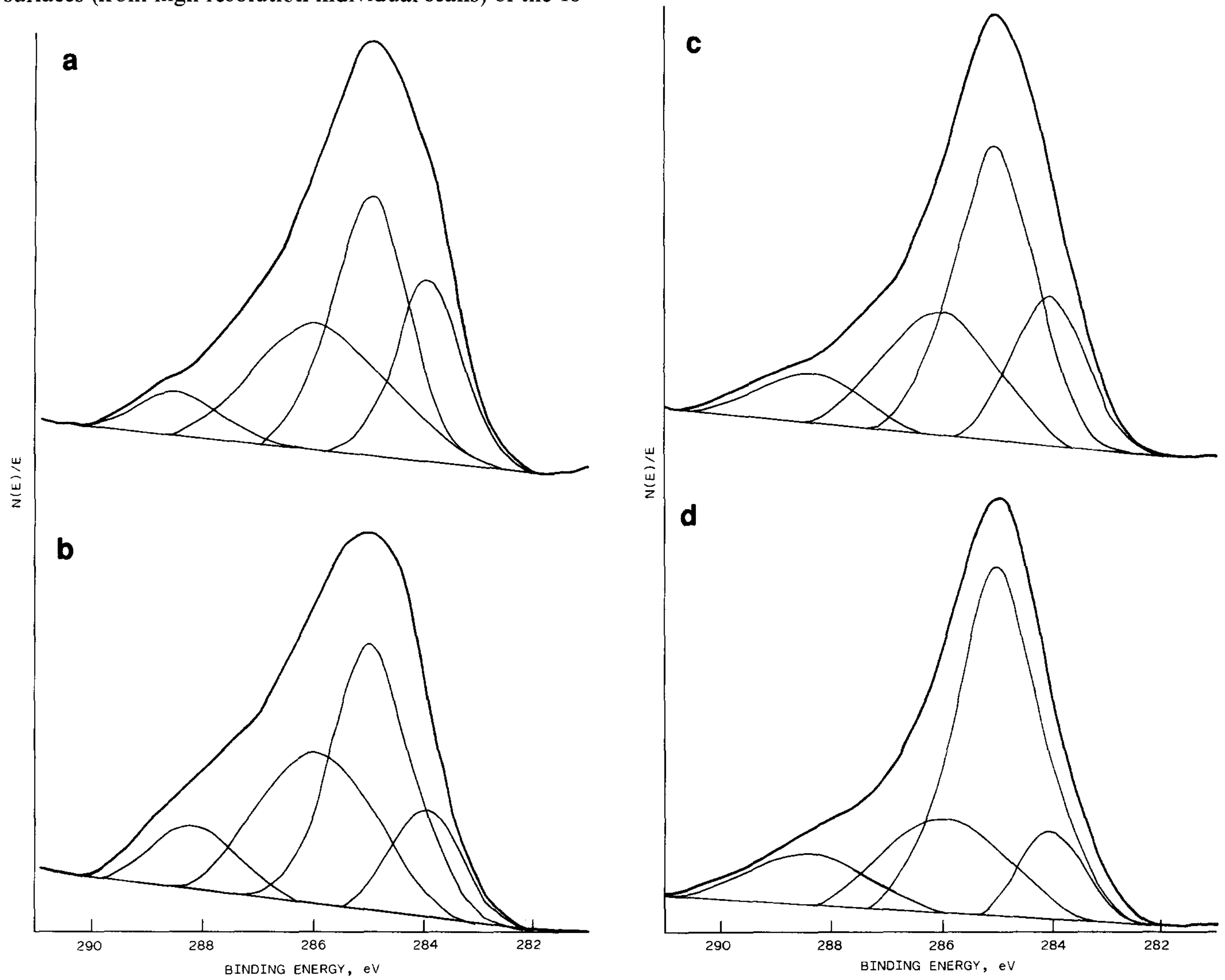


Figure 1 X.p.s. carbon 1s region curve fit analysis of BF_4 doped polypyrroles: (a) PPy face A; (b) PPy face B; (c) PPy a face A; (d) PPy a face B

Table 1 Stoichiometric atom ratios from X.p.s. surface analysis of the two faces of films PPy and PPy a and mass atom ratios from elemental analysis

Polymer	Side[a]	Atoms ratio from relative intensities of 1s level[b]	Atom ratio from relative surfaces of 1s level[b]	Atom ratio from mass elemental analysis[c]
PPy	A	$C_{5.0}N_{1.0}O_{0.7}(BF_4)_{0.2}$	$C_{5.7}N_{1.0}O_{0.6}(BF_4)_{0.2}$	$C_{4.08}H_{2.92}N_{1.00}O_{0.69}(BF_4)_{0.27}$
	B	$C_{4.0}N_{1.0}O_{1.0}(BF_4)_{0.1}$	$C_{4.6}N_{1.0}O_{0.9}(BF_4)_{0.1}$	
PPy a	A	$C_{4.7}N_{1.0}O_{0.6}(BF_4)_{0.2}$	$C_{5.7}N_{1.0}O_{0.7}(BF_4)_{0.2}$	$C_{4.31}H_{3.63}N_{1.00}O_{0.78}(BF_4)_{0.21}$
	B	$C_{4.7}N_{1.0}O_{0.7}(BF_4)_{0.1}$	$C_{5.9}N_{1.0}O_{0.7}(BF_4)_{0.1}$	

[a] Face A = Pt side, face B = growing side
[b] Sensitivity coefficients according to Reference 14
[c] Direct determination of C, H, N and O

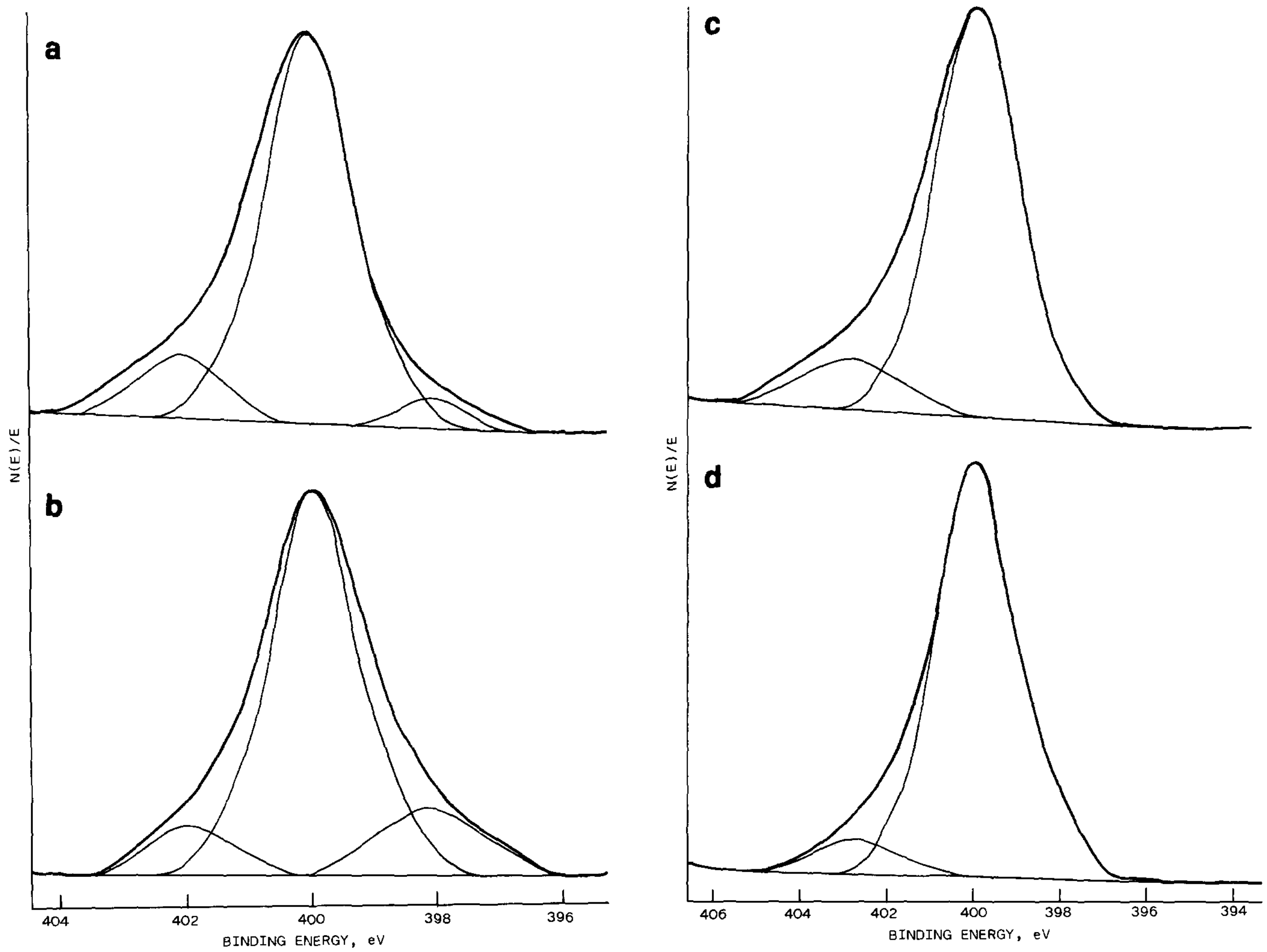


Figure 2 X.p.s. nitrogen 1s region curve fit analysis of BF_4 doped polypyrroles: (a) PPy face A; (b) PPy face B; (c) PPy a face A; (d) PPy a face B

stoichiometries compared with results from mass elemental analysis. *Figures 1–3* show the individual scans of C 1s, N 1s, and O 1s levels. The F 1s level, not reproduced in the figures, was at 685.8 ± 0.3 eV with 2.2 eV f.w.h.m. As already published[11], the separation of F 1s with respect to the B 1s level is constant at 492 eV for all samples, which means that the anion in all films and surfaces is in the form of BF_4.

Surface stoichiometry

The results (see *Table 1*) clearly show the different compositions of films and surfaces. Differences in C contents must be considered with caution, because of the coincidence of the C 1s level of hydrocarbon surface contamination with the central position of the C 1s peak of polypyrrole.

For PPy as well as for PPy a the anion content in the face in contact with Pt (face A) is higher than that in the growing solution face (face B). Similar differences in composition between film surfaces have been found for PPy by X.p.s.[10] and Auger electron spectroscopy[15]. In these studies the absence of anion has been related to the presence of dentritic areas. In fact, scanning electron microscopy (SEM) observation of similar films obtained in other solvents and using other supporting electrolytes shows that the films are less compact in the growing surface of the film. The films studied here were continuous and compact in face A and show a slightly irregular but still compact nodular (cauliflower-like) structure on face B. These results suggest that the differences in anion contents determined by X.p.s. might be attributed to a gradient in the film composition from face A to face B.

Oxygen content is higher for the growth face B, and this difference is greater for PPy than for PPy a. The difference in oxygen contents between faces can be caused either by a gradient of composition or by a different absorption of oxygen on the two sides of the film as a consequence of differences in structure. For PPy a both the oxygen content and its difference between faces is lower than for PPy, pointing to a different behaviour with respect to molecular oxygen or oxygen nucleophiles.

Carbon 1s region (see *Figure 1*)

As has been pointed out by other authors[7,11], the peak corresponding to the αC (285 ± 0.3 eV; 1.6 eV f.w.h.m.) is higher than that corresponding to the βC atoms (284 ± 0.2 eV; 1.6 eV linewidth). This has been attributed in part to structural disorder (in the βC atoms) and in part to contamination. The electron deficient C 1s species appearing at 286 ± 0.2 (2.5 eV f.w.h.m.) shows a chemical shift corresponding to C–O species. The small deconvolution bands above 288 eV could be C=O species. For PPy and PPy a the A faces are found to be very similar. C 1s differences between A and B faces are probably due

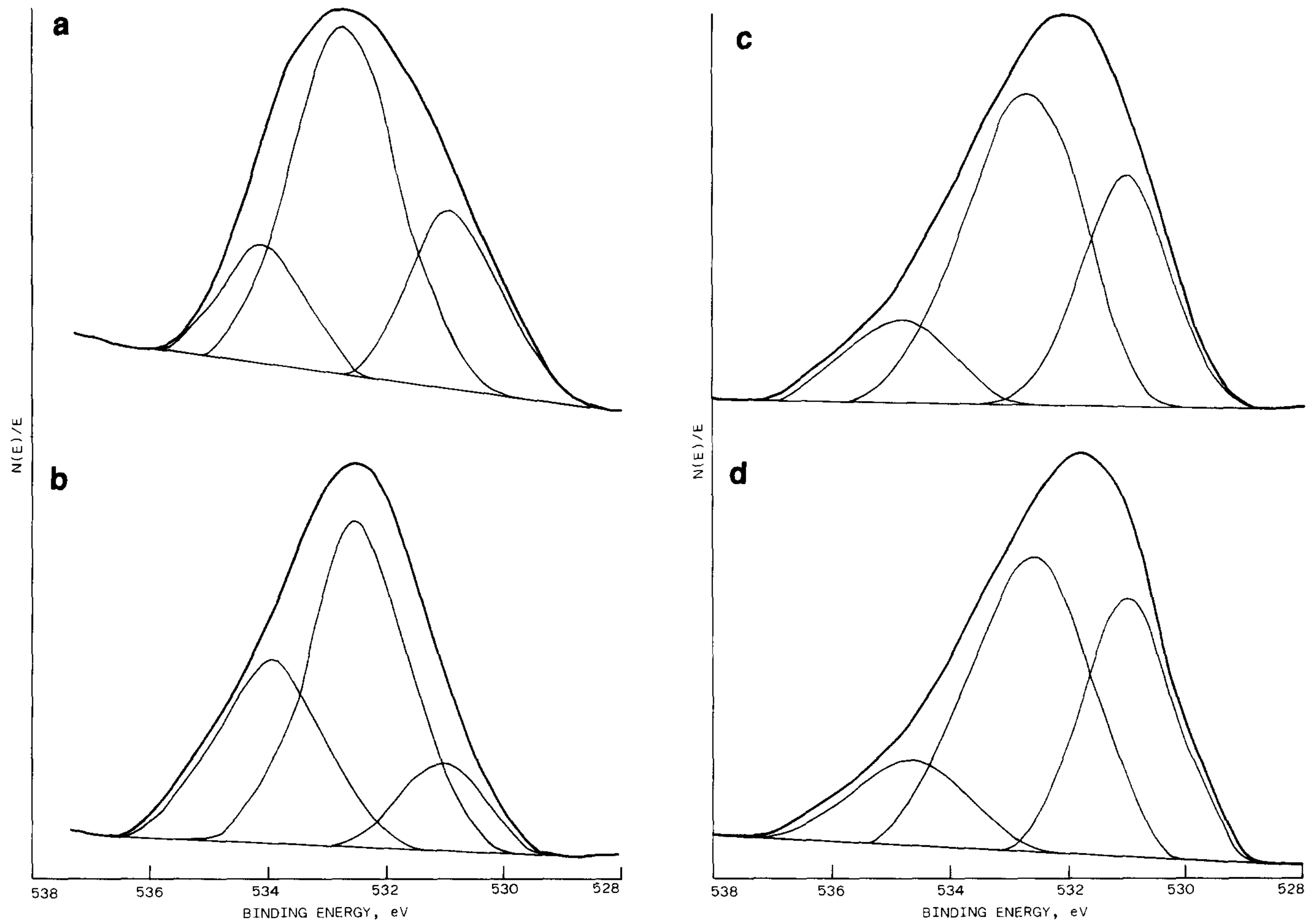


Figure 3 X.p.s. oxygen 1s region curve fit analysis of BF_4 doped polypyrroles: (a) PPy face A; (b) PPy face B; (c) PPy a face A; (d) PPy a face B

to the transformation of βC atoms into electron deficient C species, suggesting the bonding of oxygen to the βC atoms of the pyrrole rings.

Nitrogen 1s region (see *Figure 2*)

Differences between faces A and B are larger for PPy than for PPy a. In face B of PPy, the electron richer N 1s (398 ± 0.3 eV) is clearly present at higher levels than in face A. Such a difference is not observed for PPy a. Nevertheless, this result does not necessarily imply the same type of N for both faces. In this sense, note that the binding energy range between 400 and 399 eV includes several types of N 1s level: from examples of bile pigment chemistry[16–18] it is known that pyrrolic N 1s cannot be differentiated from the lactam N 1s level of 5-yliden-3-pyrrolin-2-ones (between 399 and 400 eV) and that, although the -N=C of pyrrolenic rings appears at ≈397–398 eV, on protonation it shifts to ≈400 eV. Consequently, in polypyrrole the N 1s of pyrrole rings, the N 1s of protonated pyrrolenine rings (i.e. the N of the oxidized pyrrole rings produced by doping) and the N 1s of 5-yliden-3-pyrrolin-2-one rings (i.e. for PPy a its end groups) cannot be differentiated by X.p.s. The aza species (C=N, ≈398 eV) can originate from either deprotonation of doped polypyrrole or oxidation of the already synthesized film in the absence of doping anions. In the last case, the increase of C=N species must be associated with the detection of C 1s and N 1s levels corresponding to C=O or C-O groups. The more electron deficient N species has been attributed to delocalization of electron density from the pyrrole ring associated with bipolaron formation and to the presence of N-O species[6,12].

Oxygen 1s region

Deconvolution shows that in this region there are three peaks: a central one about 532 ± 0.4 eV, an electron richer one at 534 ± 0.5 eV and an electron deficient species at 531 ± 0.5 eV. *Figure 3* shows that the faces A and B of PPy a are very similar. Face A of PPy shows the same deconvolution pattern as faces A and B of PPy a. A clear difference is shown for face B of PPy, which shows an increase in electron deficient O 1s species. Taking into account the increase of the O content of face B (see *Table 1*), the incorporated O probably corresponds to the electron deficient species, which would agree with the presence of N-O, C-O or C-O-O bonds[19,20]. The presence of such a type of bond is also in agreement with the deconvoluted peaks which appear in the C 1s and N 1s regions.

General remarks

The differences in BF_4 and O contents of both film surfaces as well as the differences in the C 1s, N 1s and O 1s levels, point to changes in reaction kinetics during the polymer growth. Other experiments under different experimental conditions show that, compared with films obtained with pyrrole alone, addition of dipyrrin-1(10H)-

ones results in less compact structures which appear progressively going from face A to face B. However, the quantitative and qualitative changes in O content are smaller for PPy a than for PPy. This fact can be explained by a higher stability of the final polymer towards oxygen. Oxygen in the films comes from two sources in addition to any deliberately incorporated species: it is incorporated in the film during its growth from the media nucleophiles (e.g. water); and it is incorporated from air in contact with the film after its preparation. Neutral and oxidized PPy takes oxygen from air irreversibly[3,6] without immediate conductivity changes. However, after some weeks in the presence of water and oxygen, a decrease of conductivity is observed[21].

Chemical reasoning on the well known behaviour of pyrrole derivatives has allowed various authors to speculate on the chemical processes involved in the interaction of polypyrrole with oxygen. The oxidized polymeric chains can undergo nucleophilic attack of oxygen nucleophilic species of the surrounding medium (e.g. water), giving C–O bonds. For C–OH bonds oxidation and prototropic processes may transform them into C=O bonds (hydroxy pyrrole derivatives transform into more stable pyrrolinones[22]): i.e. pyrrolin-3-one structures, already proposed by some authors[13,23], or pyrrolin-2-one groups in the case of an initial attack at the free α position of the end rings and in the case of attack at αC atoms followed by fragmentation processes. This explanation does not agree with the absence in the polymer of C=O bonds in spite of its high oxygen content (O:N ratios between 1:2 and 1:1; see, for example, References 5 and 13), as shown by infrared spectrometry (see, for example, Reference 8). We have confirmed the absence of significant amounts of C=O in our samples (*FT*i.r. spectroscopy in KBr), but observed strong O–H bands in spite of careful work-up procedures to exclude water in the film conservation and in the preparation of the i.r. samples. We suggest an explanation which, taking into account the isomerization of hydroxy pyrroles in pyrrolinones, agrees with all these results. Molecular oxygen, by an oxidation process through a free radical mechanism, can give hydroperoxide and peroxide derivatives attached to βC atoms: in the absence of supporting electrolyte this oxidation can also give by tautomerization N=C bonds, which in the presence of peroxides can be oxidized to N oxides. Such chemical transformation in the presence of air also explains the ageing effect of molecular oxygen or polypyrrole. Hydroperoxide derivatives of the βC atoms do not break the polyethylenic π conjugation and, in contrast with hydroxy derivatives, their evolution to pyrrolinones, which contribute to increasing the energy separation between valence and conducting bands and consequently to a conductivity decrease, is slower.

ACKNOWLEDGEMENTS

This work was financed by the CEE (project ST2J-0341), the Spanish Government (CYCIT: MAT88-0433-C03-01) and the Institut d'Estudis Catalans (IEC: programme 6023). We thank Ferran Garcia, Joan Pujades and Jordi Sauló (IEC) for their help in the preparation of samples and in computer work.

REFERENCES

1 Ribó, J. M., Dicko, A., Vallès, M. A., Ferrer, N., Bonnett, R. and Bloor, D. *Synth. Met.* 1989, **33**, 403
2 Pugh, S. and Bloor, D. *Synth. Met.* 1989, **28**, C187
3 Diaz, A. F., Castillo, J. I., Logan, J. A. and Lee, Wen-Yaung. *J. Electroanal. Chem.* 1981, **129**, 115
4 Qian, R. and Qiu, J. *Polymer J.* 1987, **19**, 157
5 Fink, J., Scherer, B., Wernet, W., Monkenbush, M., Wegner, G., Freund, H.-J. and Gonska, H. *Phys. Rev.* 1986, **B34**, 1101
6 Pfluger, P., Krounbi, M. and Street, G. B. *J. Chem. Phys.* 1983, **78**, 3212
7 Pfluger, P. and Street, G. B. *J. Chem. Phys.* 1983, **80**, 544
8 Salaneck, W. R., Erlanson, R., Prejza, J., Lundstrom, I. and Inganas, O. *Synth. Met.* 1983, **5**, 123
9 Skotheim, T. A., Florit, M. I., Melo, A. and O'Grady, W. E. *Phys. Rev. B* 1984, **30**, 4846
10 Erlanson, R., Inganas, O., Lundstrom, I. and Salaneck, W. R. *Synth. Met.* 1985, **10**, 303
11 Zeller, M. V. and Hahn, S. J. *Surf. Interf. Anal.* 1988, **11**, 327
12 Chan, H. S. O., Munro, H. S., Davies, C. and Kang, E. T. *Synth. Met.* 1988, **22**, 365
13 Cheung, K. M., Bloor, D. and Stevens, G. C. *Polymer* 1988, **29**, 1709
14 Wagner, C. D. *Anal. Chem.* 1972, **44**, 1050
15 Hahn, S. J., Gajda, W. J., Vogelhut, P. O. and Zeller, M. V. *Synth. Met.* 1986, **14**, 89
16 Falk, H., Hofer, O. and Lehner, H. *Monatsh. Chem.* 1974, **105**, 366
17 Falk, H., Grubmayr, K., Thirring, K. and Gürker, N. *Monatsh. Chem.* 1979, **109**, 1183
18 Falk, H. and Müller, N. *Mag. Res. Chem.* 1985, **23**, 353
19 Hino, S., Nakazato, M. and Matsumoto, K. *Chem. Phys.* 1988, **127**, 411
20 Clark, D. T. in 'Chemistry and Physics of Solid Surfaces', Vol. II (Ed. R. Vanselof), CRC Press, Boca Raton, Florida, 1979
21 Münstedt, H. *Polymer* 1988, **29**, 296
22 Gossauer, A. 'Die Chemie der Pyrrol', Springer Verlag, Berlin, 1974
23 Wernet, W. and Wegner, G. *Makromol. Chem.* 1987, **188**, 1465