A New Method for the Electrochemical Preparation of Highly Crystalline Poly(*p*-phenylene) Films and their Structural Characterisation

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Regular well-faceted crystals located on the inner side of homogeneous poly(*p*-phenylene) films with a relatively large degree of polymerisation have been prepared by electrochemical oxidation of benzene in concentrated H_2SO_4 without adding Lewis catalysts.

Poly(*p*-phenylene) (PPP) films, which can be produced immediately on an electrode surface by several techniques, have attracted the attention of numerous researchers because of the relative environmental stability of PPP films in the undoped state and the ability to be doped in both p- and n-directions. In addition, the polymer is extremely suitable as a model for theoretical investigations of the electronic structure of π-conjugated polymers. Two electrochemical routes are usually used for obtaining these films: (*i*) reductive coupling of dihalogenophenyl compounds in the presence of Ni^0 complexes[1] or (*ii*) oxidative coupling of the cation radicals originating from either benzene or biphenyl species in different low nucleophilic media.[2–8] The presence of Lewis catalysts in the latter case could in principle lead to some contamination of the resulting films.[9]

Here we propose a new method for the preparation of highly crystalline PPP films in concentrated H_2SO_4 without using (in contrast to ref. 8) Lewis catalysts.

The deposition of PPP films was carried out in an electrochemical cell using pure benzene in a concentrated (96%) H_2SO_4 emulsion (volume ratio 1:25) at 8 °C with continuous mixing. A piece of graphite textile or platinum sheet was used as a counter electrode. All the potentials were measured relative to a mercury sulfate electrode in concentrated H_2SO_4.

The PPP films were grafted onto thoroughly polished platinum or glassy carbon electrodes by either cycling the potential between −210 and 910 mV or by potentiostatic synthesis with an upper potential value close to 950 mV. After preparation, the PPP films were dedoped and washed consecutively with double distilled water and ethanol. Some of these films were peeled off the electrode support and then dipped into hot water (*ca.* 80 °C) with subsequent boiling in tetrahydrofuran (THF) for at least one hour.

Following this procedure, we have succeeded in obtaining PPP films with high redox activity in concentrated H_2SO_4 solution.[11] Here we report some striking features of the morphology and structure of these resulting PPP films which have been investigated in detail using scanning and transmission electron microscopy (SEM, TEM) techniques, X-ray diffraction analysis (XDA) as well as IR spectroscopy.

Fig. 1 shows a large number of regular well-faceted crystals of different sizes and thicknesses located on the inner side of the homogeneous PPP film; Fig. 2 shows typical electron diffraction patterns (EDP) obtained from these crystallites. If the electron beam was focused on the homogeneous part of the films we were able to observe diffraction rings typical of polycrystalline structures. The highly crystalline structure of the powdered film was confirmed by XDA. We have indexed the reflections using a monoclinic unit cell with parameters $a = 0.787$, $b = 0.517$, $c = 0.432$ nm and $\beta = 105.7°$. We observed single crystallites for samples treated with boiling THF, which practically excludes the low oligomer nature of these crystals. Besides, after treating the free-standing films with hot water we were able to observe the same amount of crystals under TEM as in the case of untreated samples. This seems to exclude unequivocally the observed crystals being benzensulfonic acid owing to the high solubility as well as protondesulfonation reaction of the latter in the hot water.

The length of the PPP macromolecules, resulting from possible crosslinking, which leads to the formation of some polynuclear moieties, was estimated by analysing the IR spectrum between 600 and 2000 cm^{-1} (Fig. 3). Three fundamental peaks can be clearly observed in this spectrum, the first at 807 cm^{-1}, the second between 740–761 cm^{-1} and the

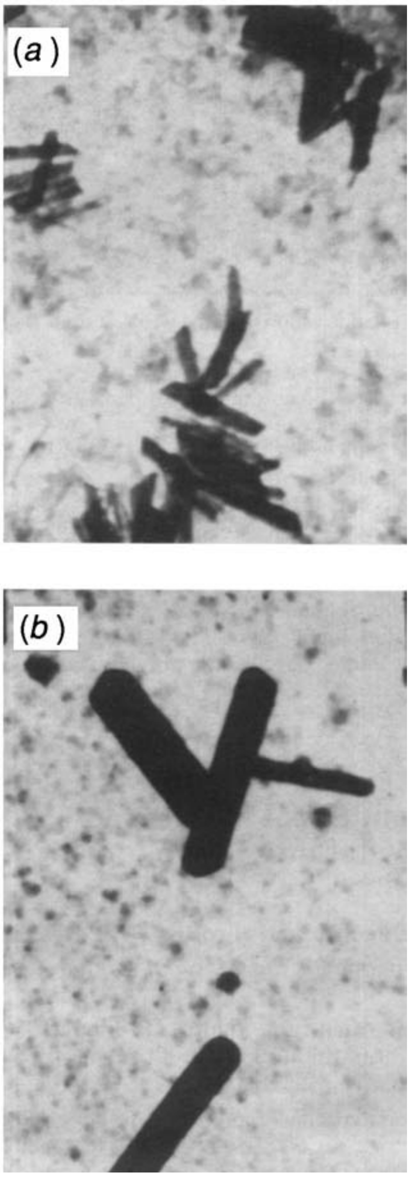

Fig. 1 Crystals of the PPP film under TEM (80 kV, multiplication ×10 000); (*a*) and (*b*) show different parts of the polymer surface

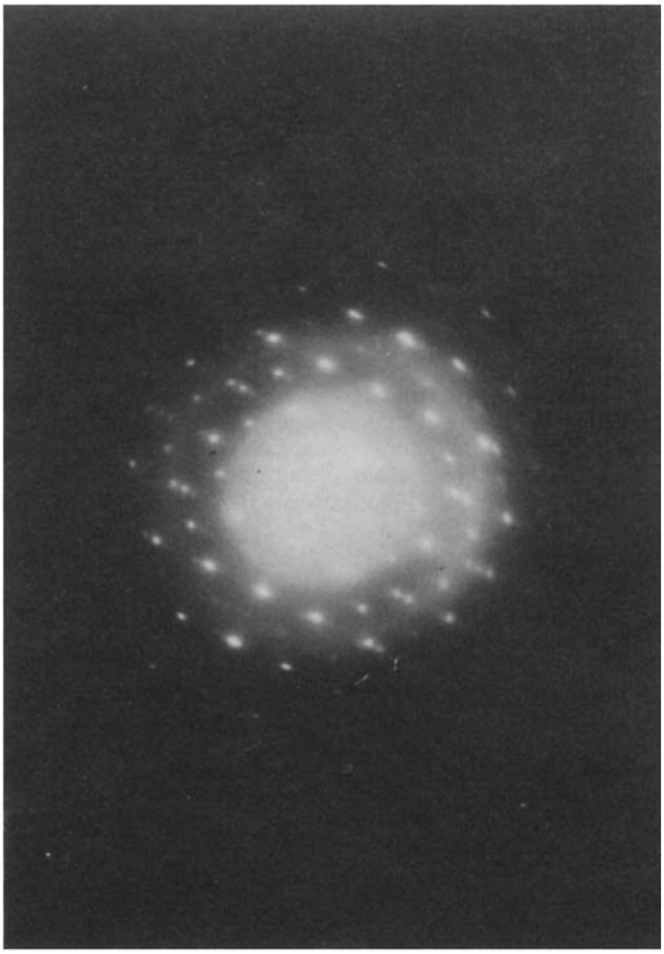

Fig. 2 Electron diffraction patterns of the crystals shown in Fig. 1

third at 690 cm^{-1}. From the ratio of peak intensities using the method of evaluation of the degree of polymerization (DP),[6,10] we conclude that DP = 29, which is a considerably larger value than that for PPP films prepared in CH_2Cl_2[5] and seems to be comparable with that for PPP obtained in liquid SO_2.[6] A peak at 1000 cm^{-1} is characteristic of *para*-substituted C_6H_4 groups, while weak adsorption peaks at 750 and 1600 cm^{-1} show the formation of polynuclear moieties to be extremely improbable.

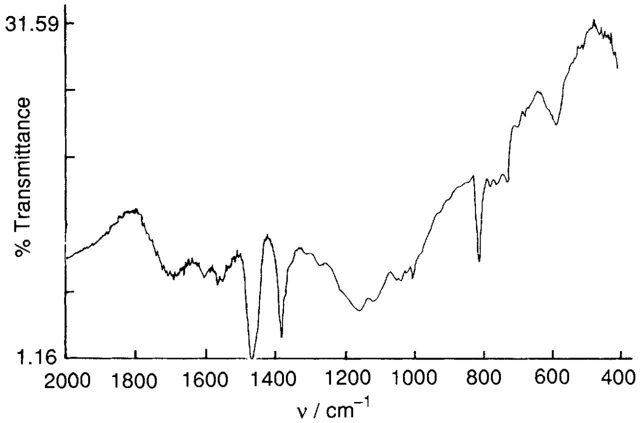

Fig. 3 IR spectrum of the PPP films in vaseline oil

In conclusion, highly crystalline PPP films, characterised by a relatively large degree of polymerisation, have been prepared in concentrated H_2SO_4 without adding Lewis catalysts. The fact that regular well-faceted crystals of PPP (some several microns in size) have been obtained seems to be a promising result for growing large macrocrystals of this polymer.

We thank Professor P. C. Lacaze, Drs S. Aeiyach and L. Goldenberg for fruitful discussions and Professors G. Tedoradze and Yu. M. Polukarov for their kind attention to the work and helpful advice.

Received, 19th July 1991; Com. 1/03709I

References

1 G. Shiavon, G. Zotti and G. Boutempelli, *J. Electroanal. Chem.*, 1985, **161**, 323.
2 I. Rubinstein, *J. Electrochem. Soc.*, 1983, **130**, 1506.
3 G. Brilmyer and R. Jasinski, *J. Electrochem. Soc.*, 1982, **129**, 1950.
4 K. Kaeriyama, M. Sato, K. Someno and S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1984, 1199.
5 S. Aeiyach, J. E. Dubois and P. C. Lacaze, *J. Chem. Soc., Chem. Commun.*, 1986, 1668.
6 S. Aeiyach, P. Soubiran, P. C. Lacaze, G. Froyer and Y. Pelous, *Synthetic Methods*, 1989, **32**, 103.
7 P. Soubiran, S. Aeiyach, J. J. Aaron, M. Delamar and P. C. Lacaze, *J. Electroanal. Chem.*, 1988, **251**, 89.
8 J. H. Ye, Y. Z. Chen and Z. W. Tian, *J. Electroanal. Chem.*, 1987, **229**, 215.
9 Toshiyuki Ohsawa, *Synth. Methods*, 1987, **17**, 601.
10 S. Aeiyach and P. C. Lacaze, *J. Polym. Sci., Part A*, 1989, **27**, 515.
11 E. Yu. Pisarevskaya and M. D. Levi, *Sov. Electrochem.*, 1991, **27**, 496.