

# Formation of surface-modified polypyrrole films by electropolymerization on non-conducting solid surfaces

J. S. Shapiro\* and W. T. Smith

*School of Chemistry, Macquarie University, North Ryde, NSW, Australia, 2090*  
(Received 8 February 1993)

Deposition of polypyrrole tosylate, synthesized potentiostatically with values of 0.5–0.8 V (relative to a standard calomel electrode) from an aqueous solution, on a solid non-conducting surface in a specially designed thin-layer cell led to the observation of two-dimensional growth of the film directly adjacent to the surface, reverting to three-dimensional dendritic growth as the film thickness increases. The significance of the two forms of morphology is discussed.

(Keywords: polypyrrole; film; morphology)

## INTRODUCTION

Since the discovery of the electrochemical oxidation/polymerization of pyrrole, resulting in detachable films of doped polypyrrole<sup>1,2</sup>, a great number of studies has been reported dealing with various aspects of the process<sup>3</sup>. While many were concerned with understanding the structure–property relationship, particularly of conductivity, and mechanical properties of the material, others dealt with the process of deposition and growth of films and the effect of synthesis conditions on the structure. These aspects are well documented in some recent publications<sup>3–5</sup>.

Examination of the morphological structures observed in doped polypyrrole using scanning electron microscopy (SEM) reveals that the films are either of an aggregated granular or dendritic appearance<sup>6–9</sup>, fibrillar<sup>10–13</sup>, or fractal<sup>10,14–16</sup>. Detailed morphology was demonstrated to depend on the nature of the electrode surface chosen<sup>6</sup> and of the counterion<sup>7,34</sup>. The solvent also plays an important role in the appearance of the film, with more compact and denser films produced in water than in polar organic solvents<sup>10</sup>. In one study, formation of films is described as taking place at the interface of two mutually insoluble liquids, resulting in very different surface characteristics for the two sides of the resultant film<sup>9</sup>. Scanning tunnelling microscopy (STM) examination of polypyrrole deposited on graphite reveals the formation of micro-islands during the initial stage of growth<sup>17,18</sup> and that isolated polymer strands display a helical structure<sup>17</sup>.

Recent publications have considered the detailed chemical mechanism of film growth on suitable electrodes, including nucleation and growth of the polymer, resulting in supramolecular dimensions<sup>19–28,31–33</sup>.

Discussions of the specific details of the film growth mechanism draw an analogy between deposition of metals and that of polymer deposition on electrodes<sup>19,20</sup>.

However, while it is perfectly clear why metallic ions would deposit themselves at cathodic surfaces, it is not so simple to account for the attraction of positively charged radical cations to the positive anode in the process of deposition of conducting polymers. This situation could arise in a number of ways. First, it is possible that the radical cations are kept in the vicinity of the anode owing to the attractive force exerted by the electrical double layer with a cloud of counterions. Alternatively, the situation could arise if the oligomeric radical ions eject protons upon their formation by oxidation at the anode at a faster rate than diffusing away. Yet another possibility is the existence of an energetic basis, as in the case of growth of polymer single crystals, when a saving in potential energy is achieved upon formation of a crystal face<sup>29</sup> or a solid film at the electrode. For non-fractal growth, film formation was found to be independent of diffusion of pyrrole to the working electrode but dependent on the dopant concentration<sup>15</sup> and to be inhibited by stirring of the solution in the electrochemical cell<sup>30</sup>.

In this paper we wish to describe an experiment that touches on the points made above, in which yet another but different method of preparation of polypyrrole (PPY) films is utilized. Our method started off as a variation of the interfacial polymerization described by Chen and Chen<sup>9</sup>, where polypyrrole was grown at the interface of toluene and water. Their experimental set-up was modified so that, while polymer deposition proceeds initially by growth on a metallic electrode, it continues to grow on a new, non-conducting solid surface, rather than at a liquid/liquid interface as described in ref. 9. This substrate on which the polymer is allowed to grow may be another polymer, or glass, or other non-conducting solid. Our films reveal on examination by SEM some new and different surface morphological features, previously only noted under conditions conducive to growing fractals<sup>10</sup>. These observations, in turn, may lead to new insights into the process of growth of conducting polymer films.

\* To whom correspondence should be addressed

## EXPERIMENTAL

Pyrrole (Aldrich) was doubly distilled immediately prior to use. Electrochemical polymerization of pyrrole (0.06–0.6 M) was carried out at room temperature in aqueous solutions of 0.5 M sodium *p*-toluenesulfonate, buffered at a pH of 5.0 with 0.3 M sodium acetate buffer. No attempt was made to eliminate oxygen from the reaction system.

Polymerization was conducted under potentiometric control using an in-house built potentiostat at potentials ranging between 0.5 and 0.8 V (*versus* standard calomel electrode (SCE)) in purpose-built single-compartment thin-layer cells. Stainless-steel square tubing (type 304, BHP Co. Ltd, Australia) internally lined with glass was used as the working electrode, with both the square electrode geometry and the glass lining serving to reduce the unwanted growth of the film towards the inner region housing the reference electrode (Standard Calomel Cell, Radiometer). *Figure 1* is a schematic representation of the thin-layer cell, with one thin-layer panel extending from each side of the square tubing. The upper wall of each thin-layer panel comprised virgin pieces of 10 mm thick poly(methyl methacrylate) (PMMA; Shinkolite-A, Mitsubishi Rayon Co. Ltd) for each experiment, with the protective masking paper being stripped off just prior to running an experiment. In most experiments the PMMA was used directly after removal of protective paper without further treatment. In some experiments the PMMA surface was wiped by a lint-free cloth moistened in 1,1,1-trichloroethane to remove residual adhesive. However, although such treatment did not significantly change the observations, it did result in formation of some fine surface scratches. A full investigation of the effect of surface pretreatment on the resultant surface morphology of the PPY is currently under way. A saturated calomel cell (K401, Radiometer Analytical A/S, Denmark) positioned inside the square tubing served as reference potential source. Epoxy adhesive (Araldite, Ciba Geigy Ltd) was used to bond glass and plastic to stainless steel during cell fabrication. Gap widths of the thin-layer cell are designated as having the thicknesses of the spacers (i.e. 50, 760, or 5000  $\mu\text{m}$ ) used during their construction.

Electrochemical reaction was allowed to proceed for 20 min or more depending on the particular experimental conditions, after which time the cell was removed from the solution and the glass base of the cell carefully split away from the remainder of the cell using a knife to expose any deposited film. Polypyrrole film adhering to the PMMA surface was carefully removed using scalpel and tweezers and purified by Soxhlet extraction in a 1:1 acetonitrile/water mixture for 1 h. Films were placed between microscope slides to reduce curling during drying in a vacuum oven at 60°C for 3 days.

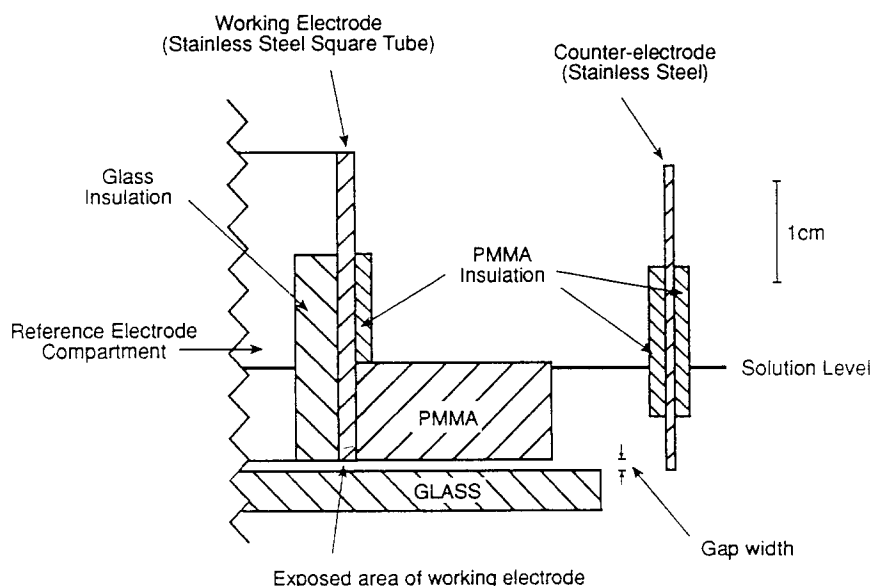
Conductivity measurements were carried out with a four-probe device built by the University workshop.

Scanning electron microscopy (SEM) was performed with a JEOL JSM-480 instrument. While the polypyrrole films were viewed microscopically directly without covering the surface with conducting material — unnecessary owing to the intrinsic conductivity of PPY — the SEM examination of bare PMMA surfaces was preceded by coating them with sputtered gold.

## RESULTS AND DISCUSSION

Using the thin-layer cell arrangement described in *Figure 1* (with gap width of 50  $\mu\text{m}$ ), it has been found that lateral growth of compact (non-fractal) films across the entire PMMA surface of the thin layer will best occur if the applied potential and pyrrole concentration are sufficiently high (>0.6 V vs. SCE and >0.6 M, respectively). At levels lower than these, lateral film deposition will either not occur, or will instead only occur as small protrusions or finger-like extensions on the PMMA surface. For this reason, an applied potential of 0.7 or 0.8 V (for 50 and 760  $\mu\text{m}$  gap thickness, respectively) and a pyrrole concentration of 0.6 M were selected as standard experimental conditions. Thus, in a typical experiment, application of 0.7 V potential to the working electrode caused rapid film growth on the exposed stainless-steel surface, followed by film growth on the PMMA surface, extending laterally (at typically an average rate of more than 0.5 mm min<sup>-1</sup>) through the narrow 50  $\mu\text{m}$  gap between the layers.

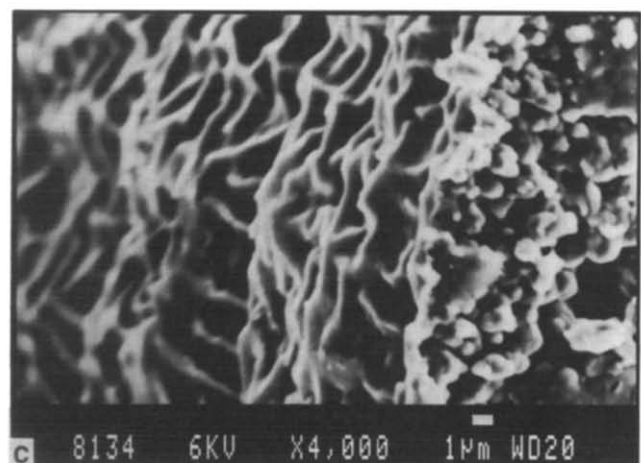
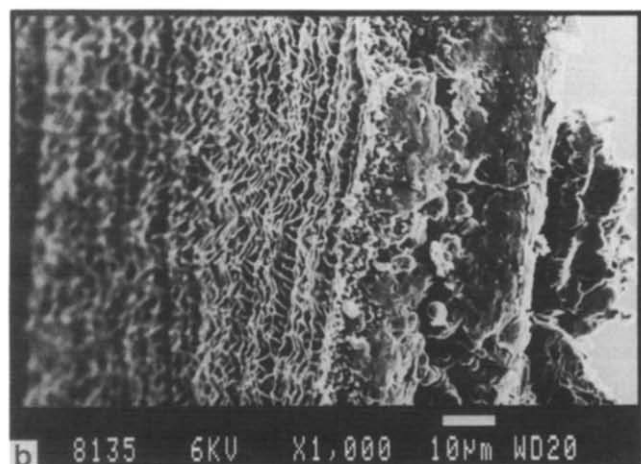
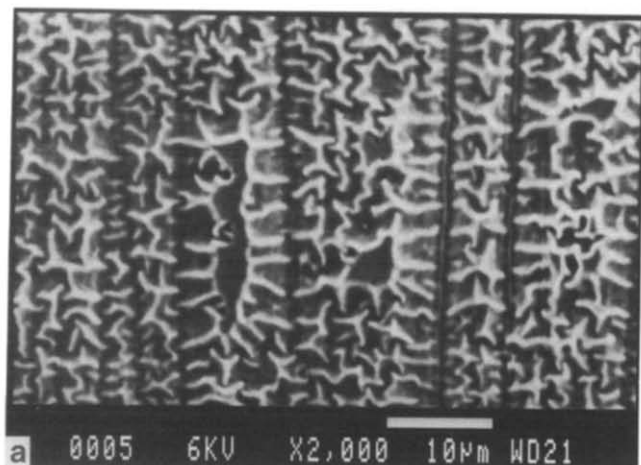
Thickness measurement of the deposited films revealed



**Figure 1** Schematic diagram of the thin-layer cell

that all were considerably thinner than the gap through which they had grown and, in the cases where wider gaps were used (760 and 5000  $\mu\text{m}$ ), films were not uniformly thick along their length but tended to be tapered towards their growing edge.

SEM examination of both sides of such films, separated from the PMMA surface, often revealed unusual features not generally reported for those grown on metallic electrodes. For example, the PMMA-facing side, whose photomicrograph is displayed in *Figure 2a*, shows a

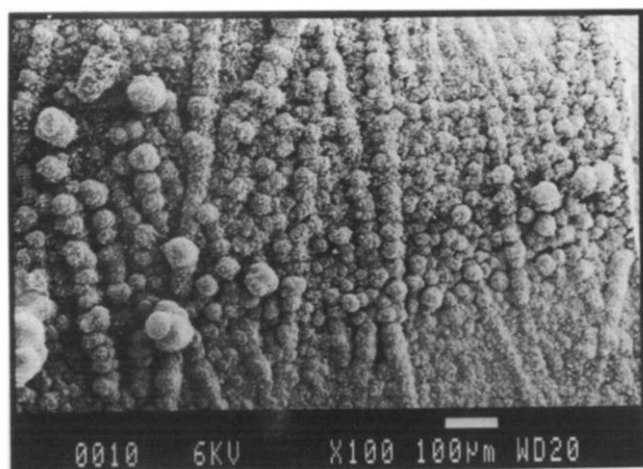


**Figure 2** SEM micrographs: (a) surface morphology of PMMA-facing surface of polypyrrole film; applied voltage 0.8 V (vs. SCE), gap width 760  $\mu\text{m}$ . (b) Oblique view of surface and edge morphology of polypyrrole film; conditions same as for (a). (c) View in (b) at higher magnification

pattern of interlaced Y-shaped markings (about 2–5  $\mu\text{m}$  in size) fairly uniformly dispersed across the surface. The appearance of gold-sputtered virgin PMMA surfaces suggests that these markings may be initiated by the replication of the underlying surface imperfections of the particular PMMA used, i.e. the PMMA surface serves as a focus for nucleation. Whether the SEM observations of surface imperfections on the virgin PMMA are real or merely due to clusters of aggregated gold used to render the PMMA surface conductive is currently under investigation.

*Figures 2b* and *2c* offer oblique views of the film produced on PMMA. On the right-hand side of the photomicrograph in *Figures 2c*, the edge of the film is seen, while the side that grew in direct contact with the PMMA surface appears on the left-hand side. A close look at the detailed honeycomb structure of the PMMA-facing side of the film shows some degree of order consistent with a two-dimensional growth. Fujii and Yoshino<sup>15</sup> have commented on the experimental conditions that they have observed and which they suggest lead to one-, two- and three-dimensional growth for experiments conducted in both aqueous and acetonitrile solutions, and they report observing similar morphology to that presented in *Figure 2c*. They noted that in acetonitrile fractal growth is promoted by very high potentials (up to 15 V, these potentials are not referenced to SCE). These workers discovered that three-dimensional fractal growth proceeds from the anode provided that the voltage is above 5 V. However, when the tip of the growing polymer approaches the surface of the glass cell or another PPY surface, the growth mechanism changes from a 3D to 2D growth pattern. In addition, they observed a quasi-1D growth, which grew along a scratch on the glass surface of their cell. It is instructive to compare the morphology of the 2D growth in the experiments reported by Fujii *et al.*<sup>15</sup> and in the present experiment, bearing in mind the great difference in the conditions under which the two morphologies were observed. The mountain-like features described by Fujii *et al.* for experiments conducted in acetonitrile are similar to the morphology observed by us, with one great difference, that in the present experiment a 2D surface appears to grow directly on the presumably inert, i.e. non-conducting, PMMA surface for a period of time, after which dendritic 3D growth is resumed. In our films, typically about 50  $\mu\text{m}$  or more in thickness, when the gap width is 760  $\mu\text{m}$ , the ratio of 2D to 3D morphology is about 1/20. In the reported experiment where water served as solvent, only 2D growth was observed by Fujii *et al.*<sup>10</sup>. However, there was no further reporting of the experiment in an aqueous environment. The morphology displayed in *Figure 2c* bears a similarity to that reported by Fujii *et al.*<sup>10</sup>. The possibility that the proximity of the glass surface in their experiments influences the nature of the film by interfering with the electric field present was mentioned by these workers. In another publication an apparent 2D morphology resembling that reported here is displayed in an SEM photograph of a polypyrrole perchlorate film prepared in acetonitrile galvanostatically on a Pt anode; however, there is no discussion or comment made on this unusual observation<sup>34</sup>.

While the electrolyte-facing side, whose photomicrograph is shown as *Figure 3*, resembles similar surfaces on films prepared on metallic anodes (e.g. ref. 7), the films



**Figure 3** SEM micrograph of solution-facing surface of polypyrrole film; conditions same as for *Figure 2*

produced in this experiment display a degree of order not normally exhibited by films grown on metals. Dendritic strands arranged in parallel lines are observed. Within each strand individual dendrites range in size from 5 to 100  $\mu\text{m}$ . Although the origin of this alignment is unclear at present, it seems unlikely that this alignment is due to nucleation at surface scratches.

It should be mentioned that replacement of PMMA with glass in the experimental set-up resulted in essentially no lateral growth through the thin-layer gap, while other polymeric surfaces such as polycarbonate, polytetrafluoroethylene, high-density polyethylene and others do promote such growth. Our observations on growth on such materials will be reported in subsequent papers. In the studies reported by Fujii *et al.*<sup>10,15</sup>, the high potentials applied to the anode were apparently necessary in order to promote a fast polymerization rate, so fast that depletion of reactants in the vicinity of the anode occurs, followed by diffusion-limited aggregation/polymerization (DLP). In the present experiment, while relatively low potentials (equal to or less than 0.8 V, reducing the extent of overoxidation of PPY) are used, it appears that our cell design leads to DLP because of the depletion of pyrrole near the PMMA surface brought about by slow diffusion within the narrow gap between the solid surfaces. Supporting this is the observation that increasing the gap width from 760 to 5000  $\mu\text{m}$  was found to result only in 3D growth.

Although the conductivity of films produced by our process is rather low (0.2–24  $\text{S cm}^{-1}$ ), especially by comparison with that reported by Chen and Chen<sup>9</sup>, it is felt that the conductivity could be improved by a considerable margin when we learn to produce films by 2D growth. Conductivity of PPY produced in our experiment is comparable to that reported by Fujii and Yoshino<sup>10</sup>.

## CONCLUSION

In summary, while we are at present unable to formulate the rules for the deposition of thick polypyrrole films via 2D versus 3D surface growth, such 2D growth has been reported previously for two very different sets of conditions from those used in this study: on metallic electrodes in aqueous<sup>10</sup> and in polar organic solvents<sup>15,34</sup>. These observations suggest, even at this early stage of limited understanding, that nucleation and

aggregation of a conducting polymer film proceeds irrespective of the method initially generating the reactive intermediates. Whereas polymeric precursors are easily formed at conducting anodes, aggregation and growth of insoluble PPY in several forms of morphology (i.e. 1D, 2D, 3D) may take place on solid or liquid non-conducting surfaces. In fact, Gregory *et al.*<sup>35</sup> have recently shown that pyrrole can be readily chemically polymerized on the surface of a range of textile fibres such as nylon-6, nylon-6,6, poly(ethylene terephthalate) and quartz. However, their paper did not display photomicrographs of the fibre/polypyrrole interface under sufficiently high magnification to determine whether 2D morphology is present. We are currently conducting additional experiments to ascertain the ideal conditions for promoting 2D morphology. It is suspected that such morphology possesses a more suitable surface than the dendritic form for practical applications such as membrane filtration and electronic device fabrication.

## ACKNOWLEDGEMENTS

Assistance generously provided by Mrs Coral Gilkeson, School of Biological Sciences, in the SEM work is gratefully acknowledged, as is the advice given by Mr Brian Hingley on the electrochemical cell design.

## REFERENCES

- Dall'Olio, A., Dascola, G., Varacca, V. and Bocche, V. C. *R. Acad. Sci. Paris (C)* 1968, **433**, 267
- Kanazawa, K. K., Diaz, A. F., Gill, W. D., Grant, P. M., Gilbert, G. B., Gardini, G. P. and Kwak, J. F. *Synth. Met.* 1979–80, **1**, 329
- Street, G. B. in 'Handbook of Conducting Polymers' (Ed. T. A. Skotheim), Marcel Dekker, New York, 1986, Vol. 1, Ch. 8
- Kim, Y. T., Collins, R. W., Vedam, K. and Allara, D. L. *J. Electrochem. Soc.* 1991, **138**, 3266
- Qui, Y. J. and Reynolds, J. R. *J. Polym. Sci., Polym. Chem. Edn* 1992, **30**, 1315
- Cheung, K. M., Bloor, D. and Stevens, G. C. *Polymer* 1988, **29**, 1709
- Cheung, K. M., Bloor, D. and Stevens, G. C. *J. Mater. Sci.* 1990, **25**, 3814
- Zinger, B., Shaier, P. and Zemel, A. *Synth. Met.* 1991, **40**, 283
- Chen, S. A. and Chen, S. H. *J. Polym. Sci., Polym. Lett. Edn* 1989, **27**, 93
- Fujii, M. and Yoshino, K. *Japan J. Appl. Phys.* 1988, **27**, L457
- Penner, R. M. and Martin, C. R. *J. Electrochem. Soc.* 1986, **133**, 310
- Cai, Z. and Martin, C. R. *J. Am. Chem. Soc.* 1989, **111**, 4138
- Martin, C. R., Van Dyke, L. S., Cai, Z. and Liang, W. J. *J. Am. Chem. Soc.* 1990, **112**, 8879
- Kaufmann, J. H., Baker, C. K., Nazzari, A. I., Flickner, M. and Melroy, O. R. *Phys. Rev. Lett.* 1986, **56**, 1932; Kaufmann, J. H., Nazzari, A. I., Melroy, O. R. and Kapitulnik, A. *Phys. Rev. (B)* 1987, **35**, 1881
- Fujii, M., Saeki, Y., Arai, K. and Yoshino, K. *Japan J. Appl. Phys.* 1990, **29**, 2501
- Atchison, S. N., Burford, R. P. and Darragh, T. A. *Polym. Int.* 1991, **26**, 261
- Yang, R., Smyrl, W. H., Evans, D. F. and Hendrickson, W. A. *J. Phys. Chem.* 1992, **96**, 1428
- Everson, M. P. and Helms, J. H. *Synth. Met.* 1991, **40**, 97
- Asavapiriyant, S., Chandler, G. K., Gunawardena, G. A. and Pletcher, D. *J. Electroanal. Chem.* 1984, **177**, 229
- Scharifker, B. R., Gracia-Pastoriza, E. and Marino, W. *J. Electroanal. Chem.* 1991, **300**, 85
- Adrieux, C. P., Audebert, P., Hapiot, P. and Savant, J. M. *J. Phys. Chem.* 1991, **95**, 10158
- Beck, F., Oberst, M. and Jansen, R. *Electrochem. Acta* 1990, **35**, 1841
- Otero, T. F. and De Larreta, E. *Synth. Met.* 1988, **26**, 79

- 24 Marcos, M. J., Rodriguez, I. and Gonzalez-Velasco, J. *Electrochem. Acta* 1987, **32**, 1453
- 25 Rodriguez, I., Marcos, M. L. and Gonzalez-Velasco, J. *Electrochem. Acta* 1987, **32**, 1181
- 26 Li, F. and Albery, W. J. *Electrochem. Acta* 1992, **37**, 393
- 27 Otero, T. P. and Santamaria, C. *Electrochem. Acta* 1992, **37**, 297
- 28 Andrieux, C. P., Aubert, P., Hapiot, P. and Savant, J. M. *Synth. Met.* 1991, **41-43**, 2887
- 29 Young, R. J. and Lovell, P. A. 'Introduction to Polymers', 2nd Edn., Chapman and Hall, London, 1992, pp. 280-285
- 30 Miller, L., Zinger, B. and Zhou, Q. Z. *J. Am. Chem. Soc.* 1987, **109**, 2267
- 31 Christensen, P. A. and Hamnett, A. *Electrochem. Acta* 1991, **36**, 1263
- 32 Waltman, R. J. and Bargon, J. *Tetrahedron* 1984, **40**, 3963
- 33 Higgins, S. J. and Hamnett, A. *Electrochem. Acta* 1991, **36**, 2123
- 34 Ribo, J. M., Tura, J. M., Dicko, A., Valles, M. A., Bloor, D., Bonnet, R. and Traveria, A. *Beitr. Electronenmikroskop. Direktabb. Oberfl.* 1989, **22**, 119
- 35 Gregory, R. V., Kimbrell, W. C. and Kuhn, H. H. *Synth. Met.* 1989, **28**, C823