

Microemulsion-based Electrosynthesis of Polyparaphenylene

K. L. N. Phani,* S. Pitchumani, S. Ravichandran, S. Tamil Selvan and S. Bharathey

Central Electrochemical Research Institute, Karaikudi 623 006, India

A new synthetic route for electro-depositing polyparaphenylene films based on an oil-in-water type microemulsion is described.

We report here the use of an oil-in-water type microemulsion for electrosynthesising polyparaphenylene (PPP) films which display electroactivity besides being electrocatalytic towards the oxidation of ascorbic acid (AA). This process is applicable to a wide variety of monomers and allows us to grow different types of conducting polymers with diverse compositions and physical properties.

While the importance of PPP is well recognised in electrochemical applications for its stability towards air oxidation and easy convertibility into n- and p-type,¹ obtaining PPP films through electrodeposition has been plagued with problems in obtaining homogeneous coherent films and high molecular mass. Further, the hitherto known methods²⁻⁸ are beset with the complicated design of electrolytic cells necessitating the

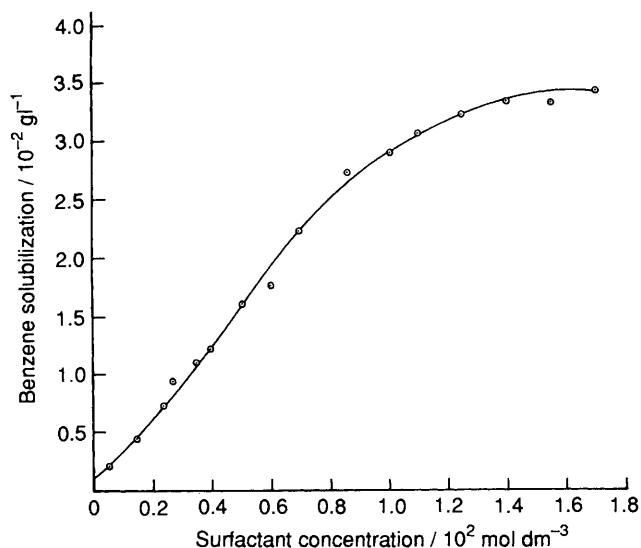


Fig. 1 Benzene solubilisation vs. surfactant concentration

use of rotating working electrode⁷ and noxious solvents.⁶ The recently reported⁹ method of synthesis with an emulsion of benzene and sulfuric acid also requires rapid rotation (2000–4000 rpm) to maintain the homogeneity of the reaction medium. Reactions carried out in this way are known to be much less efficient because of the relatively limited contact between the two phases.^{11,12}

Towards obviating these difficulties, we propose here a new synthetic approach to electrodeposited PPP films by formulating a suitable microemulsion which offers a better medium than emulsion, as the droplet dispersion is thermodynamically stable, unlike emulsion droplets, which have no place in a phase diagram. Further the microemulsions can operate as a single phase; so they do not need stirring. This approach would make large-scale electrodeposition of PPP films, an attractive proposition. Following this logic, we identify the use of an oil-in-water microemulsion of the type: benzene/concentrated sulfuric acid/sodium dodecyl sulfate (SDS). The microemulsion was prepared by adding benzene slowly to the previously prepared solution containing SDS in concentrated sulfuric acid which remains optically clear indefinitely. Although different compositions of o/w type microemulsion have been identified for this purpose as shown in (Fig. 1), the optimum composition for the electrodeposition of thick PPP film is found to be 2:5 (benzene:sulfuric acid) with a surfactant concentration of 0.15 g in a total of 70 ml of microemulsion. This was directly used as an electrolyte for the electrosynthesis thus facilitating the deposition of smooth PPP films on indium-tin oxide (ITO) glass (4 cm²) or Pt (4 cm²) when Pt plate (10 cm²) was used as the counter electrode. The electropolymerization can be carried out either galvanostatically (current density: 2 mA cm⁻²) or potentiostatically at +950 mV vs. Hg/Hg₂SO₄ (MSE) at room temperature. After each preparation, the PPP films were washed consecutively with water, ethanol and tetrahydrofuran. The film thus prepared shows good redox activity (Fig. 2) in 15 mol dm⁻³ sulfuric acid showing reversible doping/dedoping of polymer films. The potential difference between the anodic and cathodic peaks is close to 110 mV which is indicative of rather high reversibility of this redox system. The absence of H₂O-electrosorption and -desorption currents typical for the Pt substrates in sulfuric acid solutions confirmed the complete coverage of the polymer film on the electrode surface. The morphology difference observed between the Pt and ITO substrates is presented in Fig. 3 (a) and (b), which show that polymer film grown is composed of fine particles of uniform size on the ITO substrate **3a** while on Pt **3b** substrates, larger spherical particles of near-uniform size are observed. The

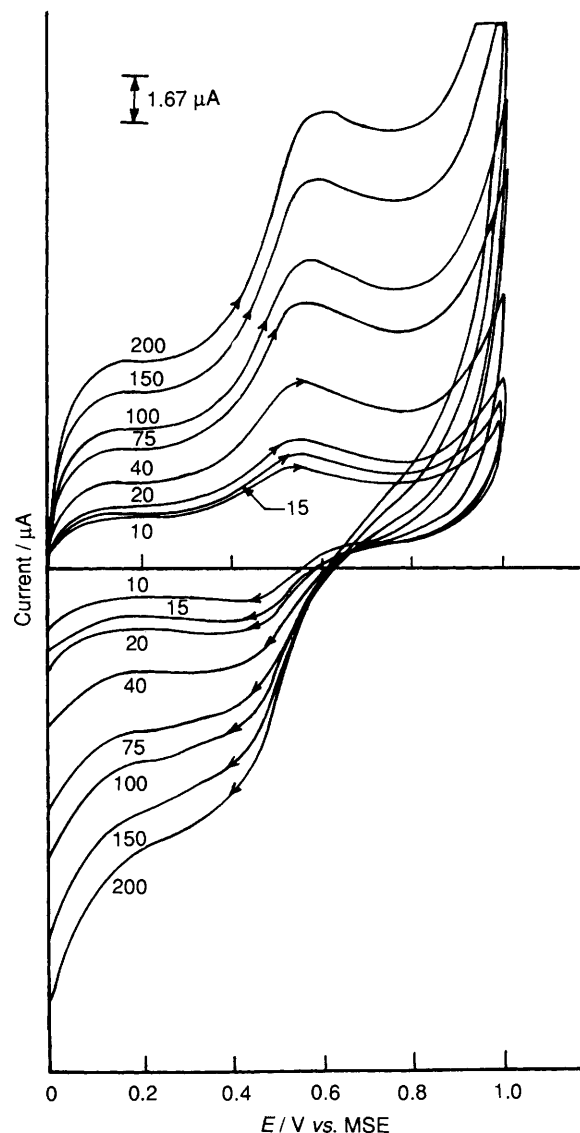


Fig. 2 Electroactivity of PPP in 15 mol dm⁻³ sulfuric acid (numbers indicate sweep rate in mV s⁻¹)

spectral data of UV-VIS and IR showed characteristic absorption peaks $\lambda_{\text{max}} = 370 \text{ nm}$ and bands at 807, 740–760, 690, 1600 and 1000 cm⁻¹, which are typical of PPP formation. The degree of polymerization estimated from the ratio of IR peak intensities based on the established procedure¹³ is found to be *ca.* 42 which is considerably higher than those obtained by hitherto reported electrochemical methods. The PPP films thus obtained also electrocatalysed the sluggish oxidation of AA. This is evident from (i) the reduction in ΔE_p value from 250 to 60 mV and (ii) a decrease in the overpotential by about 135 mV for AA oxidation in comparison to bare Pt surface (Fig. 4). It appears that the oxidation of AA is catalysed by PPP-mediated electron transfer.

Since sulfuric acid is a known⁷ strong Brønsted acid, it can protonate weak bases such as aromatic hydrocarbons like benzene thus lowering the stability of benzene and facilitates the formation of radical cations for polymerisation to proceed under the electrochemical conditions. Thus, we suggest that the electropolymerisation of benzene in concentrated sulfuric acid occurs as in Scheme 1.

As the polymerisation proceeds in the microemulsion, we believe that the microemulsion droplets reach the electrode by diffusion rather than by electrophoresis since there is no driving force for the latter process. It is not clear at present, as to the possibility of SDS incorporation into the film. However,

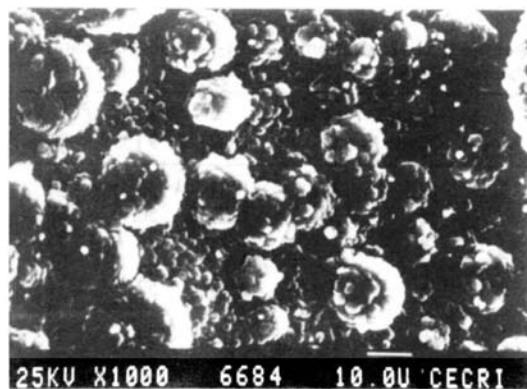
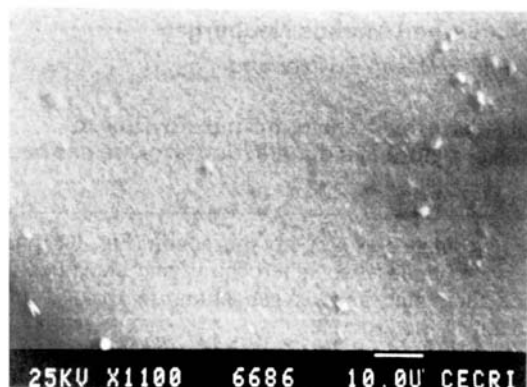


Fig. 3 SEM photographs of PPP films on (a) ITO and (b) Pt substrates

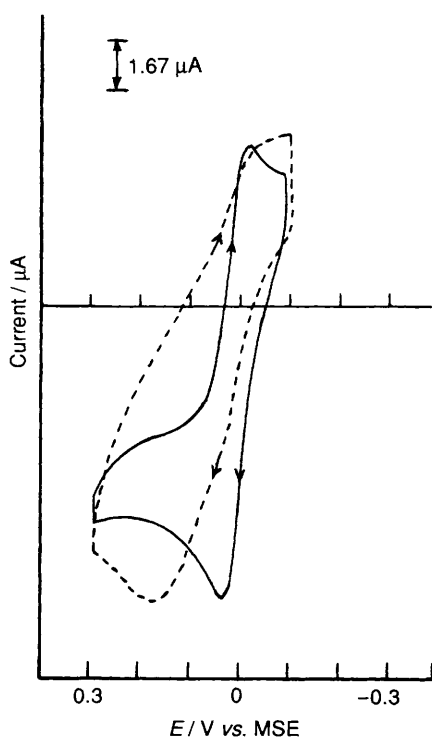
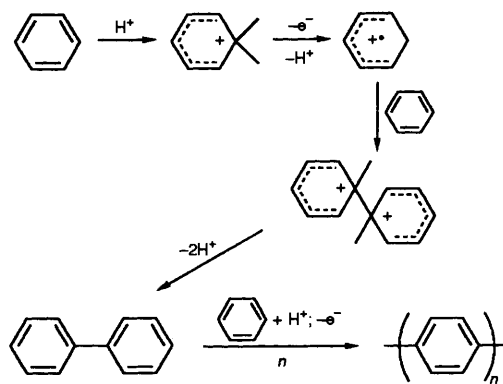


Fig. 4 Oxidation of AA in 15 mol dm^{-3} sulfuric acid solution at (---) bare Pt electrode; (—) Pt/PPP; sweep rate: 50 mV s^{-1}

(a)



Scheme 1

(b)

removal of any occluded SDS, if any, was ensured by repeated washing of the films in different solvents. If SDS forms a monolayer on the electrode surface, it may act as a template for the deposition and we are currently investigating this possibility.

This work demonstrates the remarkable influence of a surfactant in solubilizing benzene in concentrated sulfuric acid, which helps electrodeposition of PPP as homogeneous continuous films on electrode surfaces, and the very fact, that the microemulsion can be employed as a medium of electrolysis is, by its own merit, a promising result. The size that the polymer can grow to is controllable by the size of the droplet cores thus giving a much better defined range of molecular size than can be achieved using more conventional methods of polymerisation. The ability to control the electropolymerisation by microemulsion composition and the possibility of achieving crystallinity in this polymer will be described elsewhere.¹⁵

The authors thank Professor S. K. Rangarajan, Director, CECRI and Dr G. P. Rao for their keen interest in this work. S. R. and S. T. thank CSIR, New Delhi for the award of research fellowships.

Received, 9th July 1992; Com. 2/03645B

References

- 1 R. H. Baughman, in *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Marcel Decker, New York, 1986, vol. 1, p. 213.
- 2 S. Aeiyaeh, J. E. Dubois and P. C. Lacaze, *J. Chem. Soc., Chem. Commun.*, 1986, 1668.
- 3 I. Rubenstein, *J. Electrochem. Soc.*, 1983, **130**, 1506.
- 4 K. Kaeriyama, M. Sato, K. Somena and S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1984, 1199.
- 5 T. Okhsawa, *Synth. Methods*, 1987, **17**, 601.
- 6 J. H. Ye, Y. Z. Chen and Z. W. Tian, *J. Electroanal. Chem.*, 1987, **229**, 213.
- 7 P. Soubiran, K. S. Aeiyaeh, J. J. Aaron, M. Delamer and P. C. Lacaze, *J. Electroanal. Chem.*, 1988, **251**, 89.
- 8 S. Aeiyaeh, P. Soubiran, P. C. Lacaze, G. Froyer and Y. Pelous, *Synth. Methods*, 1989, **32**, 103.
- 9 M. D. Levi, E. Yu Pisarevskya, E. B. Molodkina and A. I. Danilov, *J. Chem. Soc., Chem. Commun.*, 1992, 149.
- 10 E. Yu Pisarevskya and M. D. Levi, *Sov. Electrochem.*, 1991, **27**, 449.
- 11 P. C. Hiemenz, in *Principles of Colloid and Surface Chemistry*, Marcel Decker Inc., New York, 1986, chap. 8.
- 12 J. H. Fendler, *Chem. Rev.*, 1987, **87**, 877.
- 13 S. Aeiyaeh and P. C. Lacaze, *J. Polym. Sci., Part A*, 1989, **27**, 515.
- 14 J. Facci and R. W. Murray, *Anal. Chem.*, 1982, **54**, 772.
- 15 K. L. N. Phani, S. Pitchumani, and S. Ravichandran, unpublished results.