

Chemical Synthesis of Conducting Polypyrrole and Some Composites

Vittorio Bocchi and Gian Piero Gardini

Istituto di Chimica Organica dell'Università, Via M. D'Azeglio 85, 43100 Parma, Italy

The oxidation of pyrrole to conducting polypyrrole by iron(III) salts represents a valid and more versatile alternative to the usual anodic oxidation.

Polypyrrole (PP) when obtained by chemical oxidative polymerization is a poor conducting or insulating material,^{1,2} but anodic oxidation produces better conducting films.³ Electrochemical synthesis has been recently used to produce several interesting PP-plastic composites⁴ with improved mechanical properties of the electroactive material.

This communication reports a new procedure for obtaining PP films and PP-plastic composites where the monomer is polymerised at an interface. This new procedure has the following features: (i) the products have high conductivity (in the range of 1–30 $\Omega^{-1} \text{ cm}^{-1}$), comparable with electrochemically obtained films; (ii) low cost reagents; (iii) the possibility of preparing large area conducting films; (iv) water is the main solvent; and (v) short reaction times.

Free standing PP films were prepared by room temperature contact (6 h) between a 30% FeCl_3 aqueous solution and a 10% pyrrole solution in benzene or toluene. The film formed at the interface was repeatedly washed first with water, then with acetone. Thin, flexible, and transparent films or thick, sponge-like dark brown sheets were obtained, according to the amount of pyrrole used. Pyrrole vapour may be polymerized by contact with the same oxidising solution. The conductivity range was 2–8 $\Omega^{-1} \text{ cm}^{-1}$. Analysis of a thin film gave: C, 54.95; H, 3.66; N, 15.90%; the i.r. spectrum is superimposable with the one obtained from PP prepared by anodic oxidation.⁵

Higher conductivities (10–30 $\Omega^{-1} \text{ cm}^{-1}$) were observed for composites obtained by depositing PP on one side of polyethylene films or rubber latex sheets (0.1–0.2 mm thickness). In these cases, the monomer was placed on one side of the film, polymerization being carried out on the opposite side, when the pyrrole permeated the film to come

into contact with the FeCl_3 aqueous solution.

Many other oxidizing agents such as halogens, hypohalogenides, copper(II) salts, and iron(III) salts other than chloride, etc., were tested; similar but poorer results were obtained with respect to the conductivity characteristics. The optimum reaction temperature was found to be in the range 0–10 °C.

The 'chemical' polymerization of pyrrole appears to be a general and useful tool for the preparation of conductive composites. Preliminary results show that pyrrole adsorbed onto porous materials such as polystyrene, wood, paper, cloth etc. (20–30%, w/w) may be polymerized in 60–85% yield by the oxidants mentioned here, giving composites with conductivities up to 50 $\Omega^{-1} \text{ cm}^{-1}$.

We gratefully acknowledge grants from the Italian National Research Council (CNR) and the Ministero Pubblica Istruzione.

Received, 5th September 1985; Com. 1306

References

- 1 M. Salomon, K. K. Kanazawa, A. F. Diaz, and M. Krounbi, *J. Polym. Sci., Polym. Lett. Ed.*, 1982, **20**, 187.
- 2 R. Bjorklund, H. Gustavsson, I. Lundstroem and B. Nygren, *Ger. Offen DE 3 321 281*; *Chem. Abstr.*, 1984, **100**, 87570r.
- 3 A. F. Diaz, K. K. Kanazawa and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 635.
- 4 M. A. De Paoli, R. J. Waltman, A. F. Diaz and J. Bargon, *J. Chem. Soc., Chem. Commun.*, 1984, 1015; G. Ahlgren and B. Krische, *J. Polym. Sci., Polym. Lett. Ed.*, 1984, 946; O. Niwa and T. Tamamura, *ibid.*, 1984, 817.
- 5 L. Oddi, R. Capelletti, R. Fieschi, M. P. Fontana, G. Ruani, V. Bocchi and G. P. Gardini, *Mol. Cryst. Liq. Cryst.*, 1985, **118**, 179.