1473

Poly[1,4-di-(2-thienyl)benzene]: a New Conducting Polymer

R. Danieli,^a P. Ostoja,^b M. Tiecco,^c R. Zamboni,^a and C. Taliani^{a*}

^a Istituto di Spettroscopia Molecolare, Consiglio Nazionale Ricerche, Via Castagnoli, 1, Bologna, Italy

^b Istituto LAMEL, Consiglio Nazionale Ricerche, Via Castagnoli, 1, Bologna, Italy

° Istituto Chimica Organica, Facoltà di Farmacia, Universitá degli Studi, Perugia, Italy

Electrochemical polymerization of 1,4-di-(2-thienyl)benzene leads to a new conductive polymer with an electrical conductivity of 1×10^{-4} S cm⁻¹ when doped with ClO₄⁻⁻ ions.

New conducting polymers based on heterocyclic molecular models have received a great deal of attention since the electropolymerization of polypyrrole in $1979.^{1}$ In recent years a small number of polyheterocycles have been prepared, *e.g.* polythiophene,² polyisothianaphthene,³ polythieno[3,2-*b*]thiophene,⁴ polydithieno[3,2-*b*;2',3'-*d*]thiophene,⁵ and poly(thieno[3,2-*b*]pyrrole).⁶

A twofold interest has guided this trend: the search for new materials and the need for greater understanding of the molecular factors that govern charge transport processes.

Here we report the preparation and the characterization of a new conducting polymer based on the monomer unit of 1,4-di-(2-thienyl)benzene, that was prepared according to ref. 7.

The electropolymerization is performed in a two compartment cell at room temperature with platinum electrodes



keeping the current constant. The model monomer was dissolved $(1.4 \times 10^{-3} \text{ M})$ in acetonitrile together with LiClO₄ as electrolyte (0.1 M) and the current density was maintained at 1 mA cm⁻². Under these conditions the oxidation potential stays constant at 1.06 V vs. standard calomel electrode (s.c.e.).

An homogeneous black film is formed at the anode immediately after applying current, and becomes spongy and rubbery during growth. Elemental chemical analysis agrees satisfactorily with the theoretical estimation for the molecular structure (1), with an average doping level of one ClO_4^- ion for every four monomer units.

Preliminary electrical conductivity measurements were performed in two ways: (i) by the usual four point compaction method giving a specific conductivity of 1.4×10^{-4} S cm⁻¹; (ii) a thin film of about 10 µm of thickness was grown on a high resistivity silicon single crystal electrode, made conductive by photogeneration of charge carriers. In fact during the deposition of the film, the silicon single crystal was illuminated with a tungsten-halogen lamp. As is well known, an optical excitation of sufficiently short wavelength (visible or near-i.r.) creates free charge carriers in silicon (internal photo-effect), thus increasing the electrical conductivity of the irradiated semiconductor. Dark conductivity measurements of the film were performed by using four silver paint electrodes in the Van der Pauw configuration; the specific electrical conductivity was 1×10^{-4} S cm⁻¹. The slight discrepancy between the two measurements may be accounted for by the difference in the sample treatment.

Received, 16th April 1986; Com. 505

References

- 1 A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, J. Chem. Soc., Chem. Commun., 1979, 635.
- 2 G. Tourillon and F. Garnier, J. Electroanal. Chem., 1982, 135, 173.
- 3 F. Wudl, M. Kobayashi, and A. J. Heeger, J. Org. Chem., 1984, 49, 3382.
- 4 R. Danieli, C. Taliani, R. Zamboni, G. Giro, M. Biserni, M. Mastragostino, and A. Testoni, *Synth. Metal.*, 1986, 13, 325.
- 5 P. Di Marco, M. Mastragostino, and C. Taliani, *Mol. Cryst. Liq. Cryst.*, 1985, **118**, 241.
- 6 R. Lazzaroni, J. Riga, J. J. Verbist, L. Christiaens, and M. Renson, J. Chem. Soc., Chem. Commun., 1985, 999.
- 7 P. Ribereau and P. Pasteur, Bull. Soc. Chim. Fr., 1969, 2076.