

A New Soluble and Conducting Aromatic Polymer: Poly[[1,2-(methylenedioxy)benzene]. Evidence for Partial Crystallinity

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Soluble and conducting poly[1,2-(methylenedioxy)benzene] (PMDB) films are prepared by the electrochemical polymerization of the corresponding monomer; IR and NMR studies show a *para* chain coupling for PMDB and partial crystallinity is found for the undoped polymer, using scanning electron microscopy and X-ray diffraction.

Electronically conducting aromatic polymers have been the object of a great amount of research during recent years.¹⁻³ Most of these compounds are insoluble in organic solvents, which is a disadvantage for their possible industrial applications in paints or varnishes. Recently, attempts to increase the solubility and processibility of polythiophenes and poly(*para*-phenylenes) by introducing polar groups and/or long, flexible side chains in the heteroaromatic or aromatic cycle have been made.⁴⁻¹¹ Some poly(3-alkylthiophene) derivatives were found to present a semicrystalline structure and to undergo structural variations due to alkyl side chain length and/or to dopant-ion uptake.¹²⁻¹⁵ We have electrosynthesized poly(*para*-phenylenes) and poly(naphthalenes), substituted with various size alkoxy groups, which were very soluble in usual organic solvents, but less conductive than the unsubstituted polymers.^{16,17} We have also investigated the electrochemical and photophysical properties of aromatic diethers, which can be considered as precursors for a new class of soluble polymers.¹⁸

We report, for the first time, the electrosynthesis and electrochemical study of a new soluble, aromatic polymer, poly[1,2-(methylenedioxy)benzene] (PMDB). We investigated its structure, using IR, NMR and SEM techniques and found interesting features concerning its solubility and partial crystallinity.

PMDB films were electrochemically grown on Pt electrodes from 0.1 mol dm⁻³ 1,2-(methylenedioxy)benzene (MDB) acetonitrile solutions, in the presence of 0.1 mol dm⁻³ tetrabutylammonium tetrafluoroborate (TBABF₄), tetrabutylammonium hexafluorophosphorus (TBAPF₆), tetrabutylammonium perchlorate (TBAClO₄), LiClO₄ or NaClO₄, using cyclic voltammetric, potentiostatic or intensio-static methods. PMDB films obtained potentiostatically at 1.8 V were relatively homogeneous and thick (80–120 μm).

Fig. 1 shows typical cyclic voltammograms obtained for MDB between -0.4 and 1.8 V in the presence of TBAClO₄. The voltammetric curves present several anodic and cathodic peaks in the 0.6–1.2 and the 0.65–1.05 V vs. Ag/AgCl regions, respectively. The narrow reduction peak at about 0.80 V, occurring only in the first 3–4 cycles, is probably due to the formation of aggregates growing on the Pt electrode; this peak becomes wider for a larger number of cycles, and is shifted toward small potentials, which can be attributed to reduction processes of the more homogeneous PMDB solid film. This phenomenon is confirmed by the morphological changes observed on the SEM micrographs of the film, taken at different numbers of cycles. The cathodic peak at ca. 0 V, occurring only in the presence of the monomer, results probably from the reduction of oxonium ions formed with protons after the coupling reaction. The intensity of the

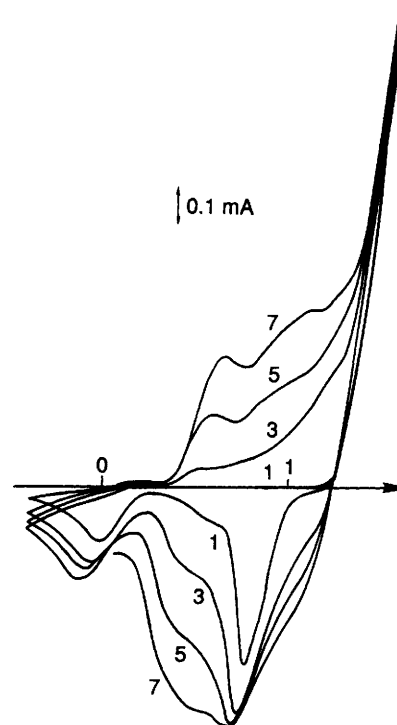
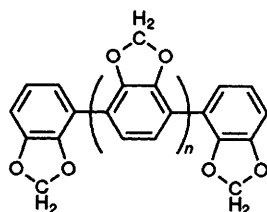


Fig. 1 Cyclic voltammograms for MDB (0.1 mol dm⁻³), recorded with a Pt electrode in a 0.1 mol dm⁻³ TBAClO₄ acetonitrile solution. The numbers labelling indicate successive potential cycles. Scan rate: 200 mV s⁻¹.

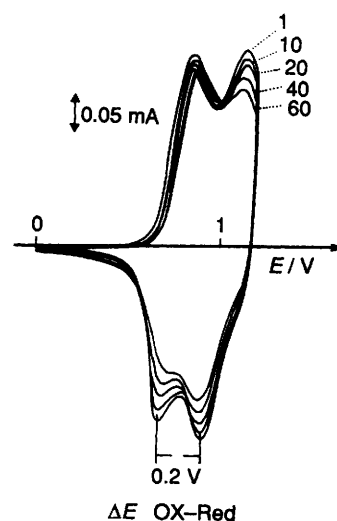


Fig. 2 Evolution of the electrochemical activity of a PMDB film, determined in 0.1 mol dm⁻³ TBABF₄ acetonitrile solution for 1, 10, 20, 40 and 60 successive potential cycles; scan rate: 200 mV s⁻¹

oxidation and reduction peaks increased regularly with the number of cycles, while a slight shift of the reduction peaks occurred towards smaller potentials, due to the formation of a conductive, homogeneous PMDB film on the surface of the Pt electrode.

To confirm the origin of these peaks and to evaluate the degree of reversibility of the PMDB redox system, we studied the evolution of the electroactivity of PMDB films in the range 0–1.2 V. As may be seen in Fig. 2, two anodic and two cathodic peaks located at 0.90 and 1.14 V and at 0.72 and 0.86 V vs. Ag/AgCl, respectively, can be ascribed to successive redox processes occurring at symmetric aromatic sites on the polymer film. The oxidation and reduction peaks are symmetrically located and are separated by differences of 0.18 and 0.28 V, for the first and second couple of peaks, respectively. The electroactivity loss (measured by the height of the anodic peak) after 60 electrochemical cycles is only about 20.7%, in the presence of BF_4^- , which indicates a relatively good reversibility of the PMDB redox system. We found also that the degree of reversibility depended of the size of the electrolyte anion (or cation). In the case of PF_6^- and ClO_4^- , electroactivity losses were 30.3 and 63.6%, respectively. This change in reversibility can be related to the sequence of ionic radii (Stokes radii): ClO_4^- (0.233 nm) > PF_6^- (0.232 nm) > BF_4^- (0.222 nm).¹⁹ Upon varying the size of the cation from TBA^+ to Li^+ , we obtained similar results, with losses of electroactivity, ranging from 63 to 19%. Therefore, use of an electrolyte with an anion (or cation) of small size is recommended in order to reach a good electrochemical reversibility of the PMDB films.

We found that PMDB in its doped state with LiClO_4 is very soluble (<18–22 g dm^{-3}) in polar organic solvents such as Me_2SO and DMF, whereas, in its neutral (undoped state), it is weakly soluble in these same solvents. This behaviour is very unusual, since most conductive polymers are only soluble in their neutral state,^{4–9,16,17} although it has been found recently that doped poly(3-methoxythiophene) and poly(3-methylthiophene) were soluble in Me_2SO and other organic solvents.¹⁰

In its neutral (undoped state), PMDB is an insulating polymer. In contrast, when it is doped electrochemically using LiClO_4 or TBAPF_6 , PMDB presents an electrical conductivity of about $5 \times 10^{-3} \text{ S cm}^{-1}$. The doping levels, evaluated by ESCA, are about 22% (ClO_4^-) and 17% (PF_6^-).

The average degree of polymerization (DP) was evaluated by measuring the molecular mass of PMDB by gel permeation chromatography (GPC), with DMF as eluting solvent. We found a DP of about 30 for PMDB. This DP value is significantly larger than the one of 13, found in the case of the 4- CH_2OH substituted derivative of PMDB.¹⁸

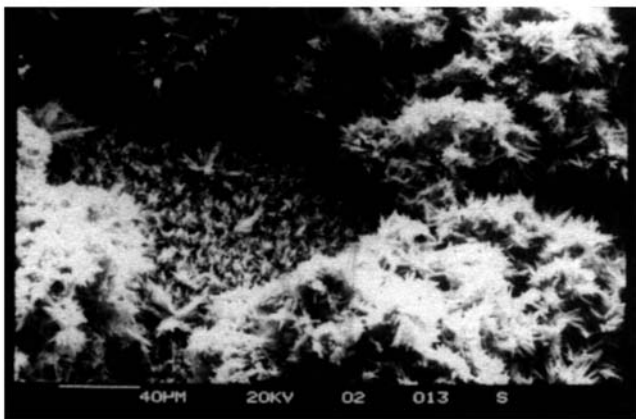


Fig. 3 Scanning electron micrographs of a PMDB film, (in the undoped state), obtained by potentiostatic electro-oxidation ($E = 1.8 \text{ V}$ vs. Ag/AgCl) of MDB in a $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ acetonitrile solution

The structure of undoped PMDB was elucidated, using FT-IR and ^1H NMR spectra. The FT-IR spectra of PMDB and its monomer, obtained in the transmission mode with KBr pellets, were compared. The diether ($\text{O}-\text{C}=\text{O}$)₂ and $\text{O}-\text{CH}_2$ stretching bands which occur at 1239 and 1041 cm^{-1} , respectively in the monomer, are shifted slightly to 1245 and 1032 cm^{-1} in PMDB, which may indicate weak steric interactions between methylenedioxy groups located on the polymer chain. The C–H out-of-plane vibrations located at 798 and 739 cm^{-1} in the monomer are characteristic of 1,2-disubstituted benzenes. In the case of PMDB, these bands disappear, as expected, and two new bands appear at 829 and 594 cm^{-1} , which are typical, respectively of a C–H out-of-plane and an aromatic ring deformation vibration for 1,2,3,4-tetrasubstituted benzenes, indicating a chain coupling in the *para* position for the polymer. In addition, it appears one band at 1164 cm^{-1} which corresponds to an aromatic $=\text{C}-\text{H}$ in-plane deformation vibration for 1,2,3-trisubstituted benzene (terminal ring of the chain). The ^1H NMR spectrum of MDB, performed in deuteriated Me_2SO , is characterized by a singlet (2H) at δ 5.98, corresponding to the protons of the methylenedioxy group and a multiplet (4H) at δ 6.88, attributed to the four coupled aromatic protons. In contrast, the ^1H NMR spectrum of PMDB, is characterized by a singlet (2H) at δ 6.17, (OCH_2O group), slightly deshielded relative to the signal of the monomer, and a singlet (2H) at δ 8.16, ascribed to the magnetically-equivalent aromatic H_5 and H_6 protons strongly deshielded relative to the corresponding signal of the monomer; it confirms the *para* chain coupling.

To determine the morphology and crystallinity of PMDB, SEM and X-ray diffraction (XRD) studies were performed, Fig. 3. When the PMDB film is in the undoped state (reduction at $E = 0.4 \text{ V}$), a crystalline, urchin-type structure can be seen on the surface of the film (Fig. 3). In contrast, the doped PMDB film is characterized by the presence of irregular granular aggregates on the surface, indicating a predominately amorphous polymer. Our XRD data confirm this difference of structure between the undoped and doped states of PMDB. Indeed, the XRD pattern of undoped PMDB presents several narrow peaks indicating a partial crystallinity of this polymer, whereas the XRD pattern of doped PMDB shows an amorphous structure.

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