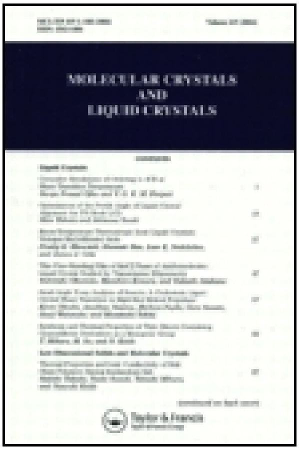

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The Fundamental Physical Properties of Poly (1,4 Dithienylbenzene) : Application to Electrochromic Displays

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THE FUNDAMENTAL PHYSICAL PROPERTIES OF POLY(1,4 DITHIENYLBENZENE) : APPLICATION TO ELECTROCHROMIC DISPLAYS.

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Abstract. The fundamental physical and electrochromic properties of electrochemically produced poly(2',2"-bithiophene)-5',5"-diyl-1,4-phenylene (PDTB) have been studied. It has been found that a wide range of film morphology can be generated through variation of deposition conditions and cell electrolyte. Seven segment electrochromic displays utilising the material exhibit good colour contrast, and perfom well even after 10^3 cycles.

INTRODUCTION.

Electrochemical polymerisation techniques have been shown to be a convenient and controllable means of producing conducting films of a wide range of aromatic materials[1]. Such films have potential applications in microelectronics, memory systems, and particularly display devices.

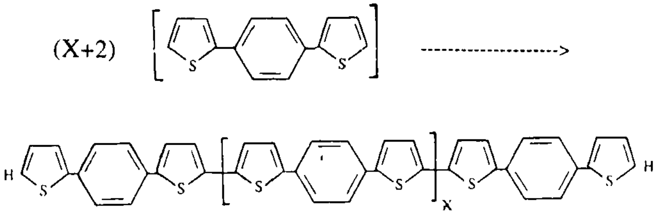
This work is concerned with the effect of variation in deposition conditions on the physical and electrochromic properties of electrochemically polymerised poly(2',2"-bithiophene)-5'5"-diyl-1,4-phenylene (PDTB).

EXPERIMENTAL DETAIL.

An A.E.G potentiostat housed in a Series 100 clean room was used to perfom the polymerisations in a standard cell under argon. A glass substrate patterned with gold (99.9999%) on chromium or doped tin oxide acted as the working electrode. An aluminium counter electrode and saturated calomel electrode were employed. The electrolytic salts used, (tetrabutylammonium hexafluoroposphate, tetrabutylammonium tetrafluoroborate, and tetrabutylammonium perchlorate), were vacuum dried at 50°C for 2 hours, while the solvent, dichloromethane, was stored over calcium chloride and subsequently filtered using 0.4μm PTFE filters. Thin films were deposited from a 0.1 M electrolytic solution containing 2g/l of 1,4,(2',2"-dithienyl)benzene using a constant current growth technique. The deposition parameters have been varied in the ranges of current densities 1-1000 μAcm^{-2} and deposition time 60-50000 seconds.

POLYMERISATION REACTIONS.

The growth rate of the films is linear with deposition time (4.2X10^{-4}μms-1μA^{-1}cm^{2}) and the polymerisation reaction is thought to proceed via a radical cation coupling process[2] as shown below.



$$+ (2X + 2)H^{+} + (2X+2)e^{-}$$

However it is clear that accompanying reactions are also prominent, forming soluble products which discolour the solvent/solute electrolyte.

RESULTS AND DISCUSSION

Physical Properties and Film Morphology.

The morphology of films grown using PF_6^- counter-ions varied considerably with deposition time becoming increasingly particulate. Films prepared under similar conditions (100 μAcm^{-2}) for differing growth times were studied using electron and optical microscopes coupled with image analysis software (Fig. 1). The particulate nature of the films increases linearly with time at a rate of 8.3X10^{-3} %s^{-1}μA^{-1}cm^{2} for growth times >120 secs as particles merge to form 'bridges' and then a conglomerated mass covering ~92% of the film area. A gravimetric method was used to measure film density and this was found to be 1.28 gcm^{-3} independent of deposition time, suggesting that when present, particulates exhibit a high packing efficiency. Light element analysis suggests that the counter-ions are evenly distributed across the film and not distributed in areas of particulate development.

Electrochemically produced polymers are composite materials containing counter-ions from the electrolyte. These ions can influence the polymerisation and thus film morphologies by either a steric or an electronic effect[2,3]. Indeed we see a considerable variation of morphology in films grown using identical conditions (500μA for 240secs) except for choice of counter-ion. (Fig.2). Films containing ClO_4^- ions show the highest concentration of particles and those containing BF_4^- ions the lowest. The underlying fibrous structure is similar in all cases. The film densities are also counter-ion dependent, being 0.98 gcm^{-3} for those containing ClO_4^- ions and 1.16 gcm^{-3} for those containing BF_4^- ions.

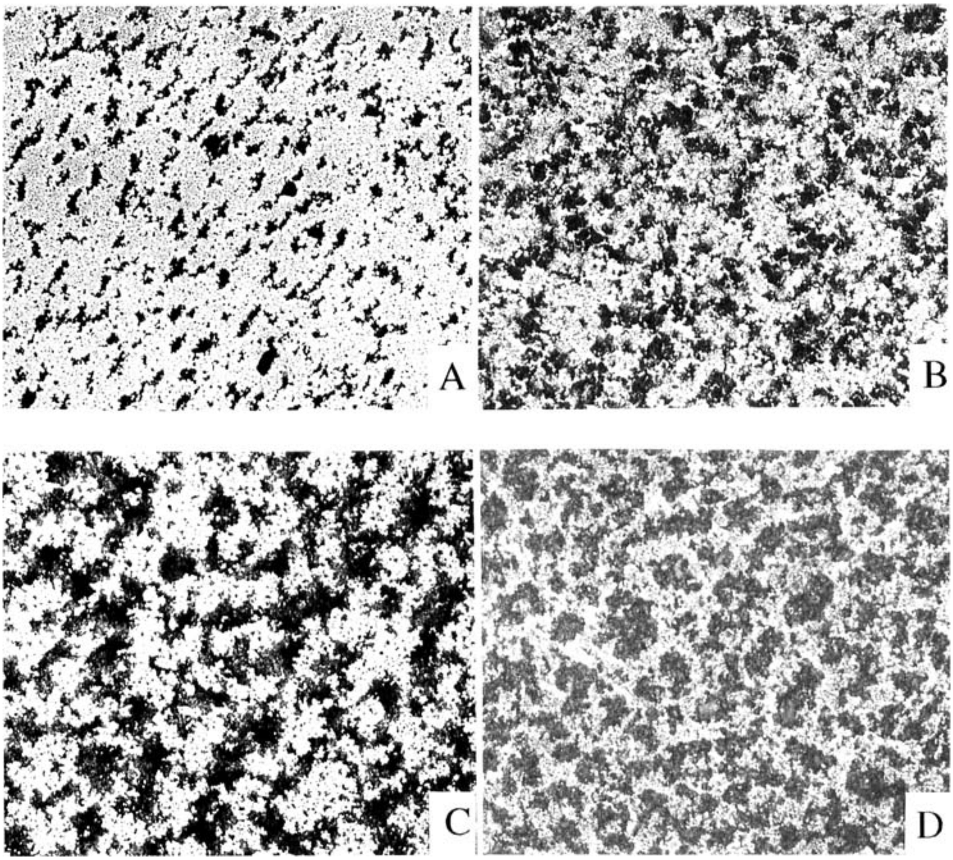


FIGURE 1. The surface morphology of 4 Poly PDTB/PF_6^- films deposited for various times: A) 4 mins. B) 8 mins. C) 12 mins. D) 16 mins. (Mag. X80)

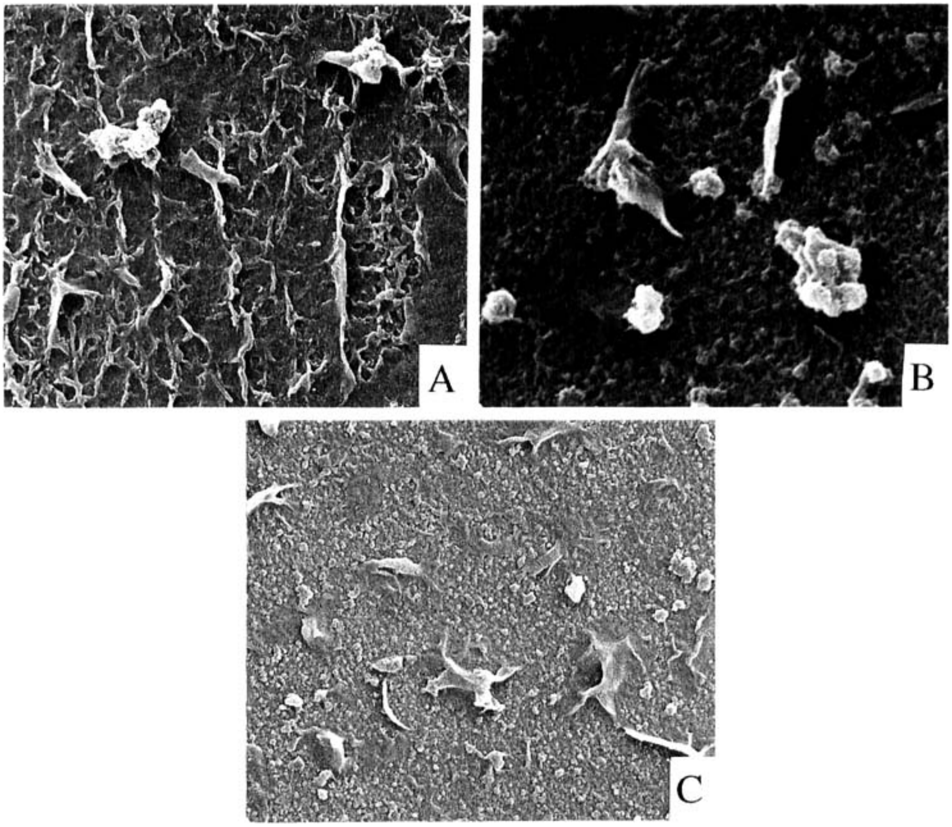


FIGURE 2. The Surface Morphology of three PDTB deposited using various electrolytic salts. The counterion in each case is A) PF_6^- , B) BF_4^- , C) ClO_4^- (Mag X 5400).

Electrochromic Properties.

A range of electrochromic organic materials, including viologen[4], and more recently substituted thiophenes[5], and polyanalines[6] have been studied with a view to developing new types of display devices.

PDTB is an electrochromic material exhibiting a reversible change between it's oxidised (dark blue) state, and its reduced (amber) state. This transition can be studied by noting the change in optical density defined[7]as the ratio of the transmitted light (Tc) in the coloured and (Tb) bleached state according to dOD=log(Tc/Tb) as a function of applied potential.(Fig 3.). The films were held at each potential for 900 secs to ensure that all active colour centres had changed state before measuring their O.D. Despite the lack of a well defined oxidation potential (Fig. 4) the transition between the states occurs sharply at 1.5V vs S.C.E. This is in contrast to the gradual changes commonly reported[8,9]. The lifetime of the colour change can be estimated from cyclic voltammograms over many cycles. Such studies of PDTB show considerable initial decay in the optical activity of the film, which is associated with the leaching of oligomers from the film. This is followed by a less significant decay process which results in small areas of the film remaining unchanged. This probably indicates poor adhesion to the substrate at these points[10]. Despite this, the films retain >50% of their original activity after 10^3 cycles and appear to switch to the naked eye. Further work is underway to study the effect of variations in morphology on display performance . Complementary studies on polysiloxanes have indicated a significant dependence on such effects[11].

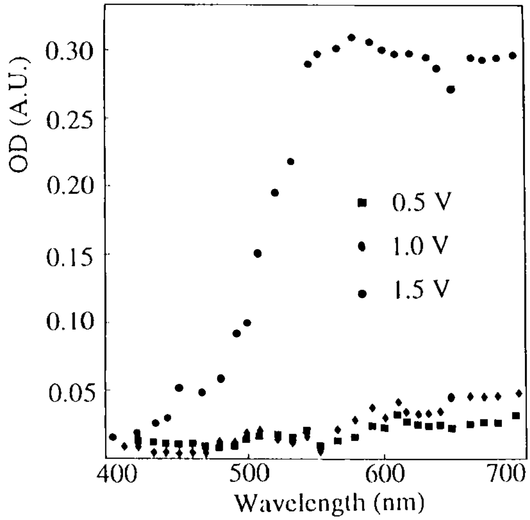


FIGURE. 3. Change in Optical Density of a PDTB/PF_6^- film with respect to the neutral state as a function of applied electrode potential . (All potentials vs S.C.E)

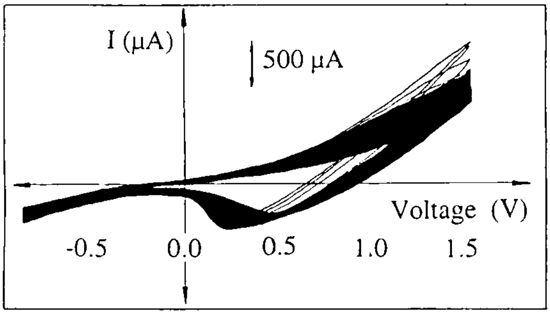


FIGURE.4. Typical cyclic voltamogram of a PDTB/PF_6^- film cycled 10^3 times at 200 mVs^{-1}.

Electrical Measurments

D.C conductivity measurments have been restricted due to the uneven nature of the growth process which results in areas of very high electric field and breakdown. It is only possible to conclude that the high field conduction approximately follows the temperature and field dependence of disordered polymer systems, and that the current densities measured for the oxidised state are>1000 times those measured for the reduced state.

CONCLUSIONS

It has beeen observed that the morphology of PDTB films is highly dependent on both deposition conditions and cell electrolyte. Further work is underway to assess the effect of these factors on prototype seven segment displays which preliminary studies suggest perform well, even after 10^3 cycles.

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