

Medium Effect on the Anodic Fabrication of Poly-(*p*-phenylene) Films on Platinum Electrodes

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The acidic-basic properties of the medium, its water content, and the nature of the anion of the supporting electrolyte are the main physicochemical parameters affecting whether homogeneous, adherent, and conductive poly(*p*-phenylene) films are obtained from electrochemical oxidation of benzene or biphenyl; use of a strictly anhydrous solvent such as CH_2Cl_2 or MeNO_2 without a catalyst leads to conductive ($\sigma > 1 \text{ S cm}^{-1}$) and electrochromic films with BF_4^- , PF_6^- , or SbF_6^- anions, while insulating films are formed with ClO_4^- anions.

Recently, several techniques have been proposed for the electrochemical formation of poly(*p*-phenylene) (PPP) films from benzene or biphenyl. Although some are based on reductive coupling of dihalogenophenyl reagents catalysed by Ni complexes,^{1,2} most involve oxidative coupling of cation radicals, for which different media have been used: *e.g.* $\text{HF} + \text{C}_6\text{H}_6$,³⁻⁵ $\text{SbF}_5 + \text{HF} + \text{C}_6\text{H}_6$,⁶ MeNO_2 or $\text{PhNO}_2 + \text{C}_6\text{H}_6 + \text{AlCl}_3 + \text{Bu}_4\text{NClO}_4$,⁷ and, recently, PhNO_2 or $\text{PhCN} + \text{C}_6\text{H}_6 + \text{LiAsF}_6$ including the co-catalyst CuCl_2 .⁸ We now show that plastic, homogeneous, and surface-adherent electroactive PPP films may be synthesized by direct oxidation of benzene or biphenyl using a classical but strictly dry organic solvent containing an electrolyte with F atoms.

Generally speaking, it is possible to obtain either an insulating or a semiconductive film by oxidation of benzene or biphenyl. When the film is conductive its thickness increases with the number of polarographic cycles. Sometimes the polymer does not adhere to the electrode surface, and in this case the electrolysis yields black filaments which diffuse through the solution. All these phenomena depend on the type of electrochemical medium.

In studies on the effect of water content, film formation was not observed for water concentrations $> 10^{-2} \text{ M}$. In Bu_4NBF_4 (0.1 M) in CH_2Cl_2 containing a water concentration of about $2 \times 10^{-2} \text{ M}$, no film was formed and black filaments diffused from the working electrode towards the bulk of the solution. Addition of P_2O_5 in excess (200–400 mg in 25 ml of solution) led to strictly anhydrous media (no water could be detected by the Karl Fischer technique), and the oxidation of benzene or biphenyl led to homogeneous films, whose thickness increased with the number of sweeps. The same effect was observed on addition of molecular sieves (4 Å) to the electrolysis solution, which also led to rigorously anhydrous media. The oxidation

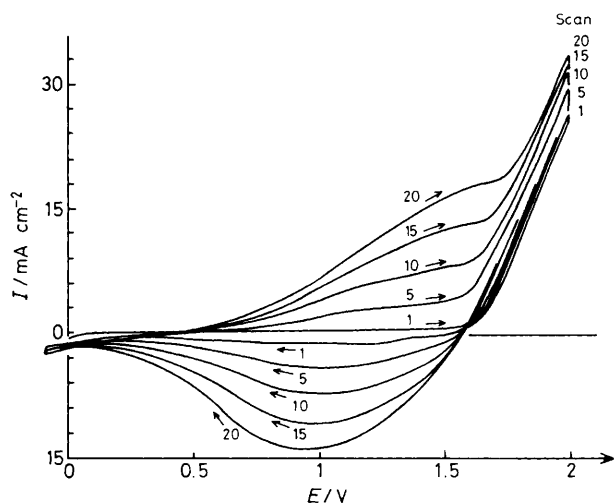


Figure 1. Film growth on Pt during repeated potential scans between +2 and -0.1 V vs. Ag-AgCl (scan rate 100 mV s^{-1}) in CH_2Cl_2 (25 cm^3) + 0.1 M Bu_4NPF_6 or 0.1 M Bu_4NBF_4 + P_2O_5 in excess (200–400 mg) + biphenyl ($1.3 \times 10^{-2} \text{ M}$).

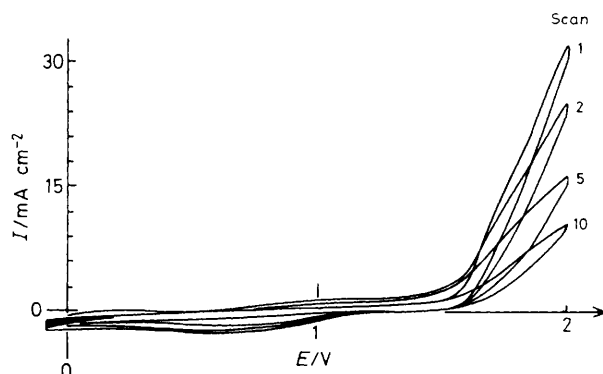


Figure 2. As for Figure 1, but with ClO_4^- anion instead of BF_4^- or PF_6^- .

of benzene yielded a conductive film similar to that obtained in the presence of P_2O_5 .

In neither case were filaments formed, the polymer appearing only on the electrode surface giving a homogeneous film. However the two means of making the medium anhydrous give chemically distinct results. A highly acidic medium (pH ~ 1) was obtained using an excess of P_2O_5 , while the addition of molecular sieves led to a neutral medium (pH ~ 6). In acidic media the oxidation of benzene or biphenyl is easier, owing to protonation of the aromatic rings. As a consequence, the i - E curves in acidic media are shifted towards less anodic potentials (-0.5 V).

With regard to salt and solvent effects, when 0.1 M Bu_4NClO_4 was added to the solvent (CH_2Cl_2) saturated with P_2O_5 the oxidation of benzene or biphenyl led to an insulating film and no electrochromic effect was observed. In contrast, use of BF_4^- , PF_6^- , or SbF_6^- instead of ClO_4^- as anion gave a conductive adherent film, which was partially crystalline (Figures 1 and 2). A similar phenomenon was observed for liquid SO_2 media.⁹ The use of slightly acidic solvents such as CH_2Cl_2 or $MeNO_2$ made film formation easier. In contrast, $MeCN$, which can be considered to be more basic than the other solvents, led to less homogeneous films with poor adherence. The acidity of the medium also has an important effect on film adherence on Pt. According to the adhesion theory of Fowkes, which involves acidity and basicity parameters,¹⁰ it appears that suitable conditions for the adhesion of aromatic nuclei (considered as slightly basic) on a metallic surface are fulfilled in acidic medium.

All the films were characterised by i.r. absorption bands at 812 , 752 , and 696 cm^{-1} , the intensities and positions of which are quite similar to those of *sexi-p*-phenylene¹¹ and confirm that PPP structures had been obtained.

Oxidation-reduction of the electroactive films led to a strong reversible electrochromic effect. During the oxidation,

for potentials >1.2 V a green colour gradually appeared on the surface and the layer blackened for potentials >1.8 V.

The films were bleached at potentials between 1 and 0.7 V, but retained the pale green colour characteristic of the neutral film. The superficial layer of the film is composed of homogeneous grains (size ~ 5 μm). The superficial layer can be removed by thorough ultrasonic rinsing in acetone, to leave a very homogeneous, 0.5 μm thick golden layer adhering to the surface.

The conductivities of the films vary between 10^{-3} and 1 S cm^{-1} and depend on the experimental conditions used in their fabrication.

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