

Electrochemical Syntheses of Condensed Ring Conductive Polymers using an Ambient Temperature Molten Salt

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Benzene and other aromatic hydrocarbons can be anodically polymerised to give a highly conducting polymer film at a potential of 1.5 V and below, using a chloroaluminate melt consisting of a mixture of cetyl pyridinium chloride and aluminium chloride containing benzene at room temperature; the 10 μm thick polybenzene film thus obtained has a conductivity of more than 10^4 S cm at 290 K.

Although various methods are known for the preparation of poly(*p*-phenylene) (PPP) and various other conducting polymers,¹⁻³ none of them produces highly conducting polymers owing to defect-related limitations on the effective conjugation length. Any improvement in conjugation length, structural order, and chain alignment may dramatically improve the electrical conductivity and mechanical properties of PPP.⁴

To obviate these difficulties to a certain extent, we explored the new room temperature melt obtained by mixing freshly sublimed anhydrous aluminium chloride (67%, 2 mol) and cetyl pyridinium chloride (CtPyCl) (33% 1 mol). The mixing can be carried out with ease if the required amount (50% v/v) of benzene is mixed with CtPyCl prior to the addition of AlCl_3 in parts to avoid increasing the temperature. This procedure gives a very clear solution. When the melt is subjected to electrolysis between a Pt or an indium-tin oxide (ITO) anode and a Pt cathode at 1.5 V against aluminium wire as a reference electrode, a thin and rigid semi-transparent reddish brown film is obtained on the anode surface and the cetyl pyridinium cation is discharged at the cathode producing a transparent gelatinous mass after prolonged electrolysis. The rotating-ring disc experiments gave E_1 for polymer deposition at 1.20 V against an Al wire electrode with a limiting current at 1.25 V.

The polymer (PPP) was deposited as a thin film (10 μm) on the anode surface and after washing with dry benzene showed a conductivity of 10^4 S cm at 290 K (using a d.c. four probe method).

Elemental analysis of the freshly prepared polymer gave C

54.5%, H 3.2%, Al 6.8%, and Cl 35.3 which amounts to a dopant concentration of 42% by weight. This gives the stoichiometry of the polymer to be $(\text{C}_6\text{H}_4)_3\text{AlCl}_4$ which suggests that the polymer-cation chain becomes stabilised by removing AlCl_4^- .

If benzene is replaced by a halogenobenzene the electrolyte immediately turns a light brown colour and polymerisation is eventually prevented. This is due to the formation of a

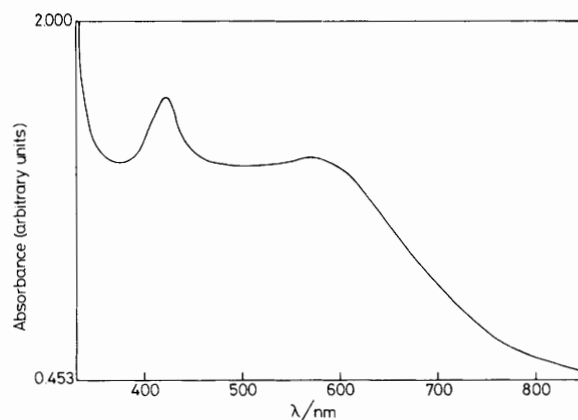


Figure 1. Diffuse-reflectance u.v./vis spectrum of the benzene polymer (film on Pt).



Figure 2. Scanning electron micrograph of the polymer, showing at least one superstructure.

halogenobenzene radical cation *via* a dissociative mechanism, which releases the halogen, thereby allowing preferential adsorption of halogen at the anode surface.

However, we concentrated on the study of benzene polymerisation. The diffuse-reflectance u.v./vis spectrum (Hitachi- U 3400) of the benzene polymer showed a well defined band having λ_{\max} 421.8 nm and a broad shoulder at 564.5 nm (Figure 1). PPP, prepared by the Kovacic method,⁵ containing 16 phenyl rings, exhibits λ_{\max} at 363 nm. This suggests that polymerisation *via* the method described is extensive. A molecular weight determination of the polymer

was hindered by its insolubility and its infusible nature. We found it extremely difficult to grind the polymer with KBr for i.r. spectroscopic studies; however, an old sample gave very weak absorption bands at 1390, 1480, and 3400–3000 cm^{-1} . The scanning electron micrograph (SEM) (Figure 2) reveals that the film is uniform and in one small region may contain at least one super structure.

Polymerisation of pyrrole, diphenylamine, anthracene, and naphthalene diluted with benzene was also performed. Pyrrole and diphenylamine gave bright blue and green films with conductivities of 10^3 S cm and 67 S cm respectively. Anthracene and naphthalene gave brown films with conductivities of 1 and 0.8 S cm respectively. Both pyrrole and diphenylamine concentrations were kept at 1×10^{-2} M because of their tendency to form complexes with AlCl_3 present in the electrolyte.

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