Electrochemical Preparation of Poly(pyridazine)

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A poly(pyridazine) film which is blue in colour with an electrical conductivity of 10 S/cm has been obtained, for the first time, by the electrochemical oxidation of pyridazine.

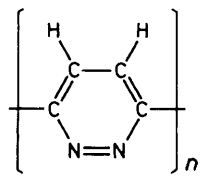
New conducting polymers with conjugated double bonds have attracted much attention recently as they display various interesting phenomena. The electrochemical preparation of conjugated polymers is a useful method of obtaining highly conductive and flexible films. Many attempts have been made to produce new conducting polymers, but only a limited number of polymers such as poly(pyrrole),[1] poly(thiophene),[2—4] and poly(selenophene)[5] have been synthesized by this method.

Here we report the electrochemical preparation and properties of a new type of conducting polymer, poly(pyridazine).

The electrochemical oxidation of pyridazine was performed in a one-compartment cell at room temperature using an ITO (indium tin oxide conducting glass) anode and a Ni cathode. When potentials of *ca.* 4—8 V were applied between the two electrodes immersed in a solution of pyridazine (0.4 mol/l) in benzonitrile containing an appropriate electrolyte such as $LiClO_4$ (0.2 mol/l), a blue film was obtained on the ITO electrode. The typical current density observed in this polymerization was *ca.* 1.5 mA/cm^2 at 4V. Alternative combinations of solvent (acetonitrile, propylene carbonate, and nitrobenzene) and solute ($LiBF_4$, $LiAsF_6$, and NBu_4ClO_4) give similar films. However, the solution of $LiClO_4$–benzonitrile was found to be the best for obtaining a high quality film at this stage of the experiment.

Poly(pyridazine) polymerized on an anode electrode surface, contains the acceptor dopant (*e.g.* ClO_4^-). The dopants can be removed either by applying a negative voltage with the polymer as cathode or by washing with NH_4OH solution to give the neutral form of poly(pyridazine).

Chemical elemental analysis agreed satisfactorily with theoretical estimations for the molecular structure (**1**). The i.r. spectrum shows that the polymer has peaks at 1583, 1550, 1457, 1049, 980, and 704 cm^{-1} originating from the pyridazine ring and also peaks at 1122, 1089, and 881 cm^{-1} derived from *para* substituted pyridazine. These results are consistent with the molecular structure (**1**). These results indicate that electrochemical reaction of pyridazine is preceded by the



(1)

removal of the hydrogen from the carbon atoms of pyridazine next to nitrogen.

The colour of the doped film is blue. On the other hand, the neutral film is brown in colour with an optical absorption edge, corresponding to the band gap energy of poly(pyridazine), which is *ca.* 1.8 eV.

The electrical conductivity of poly(pyridazine) prepared as described above was 10 S/cm and the activation energy of the conductivity is estimated to be 0.02 eV at room temperature, which coincides with the value for doped poly(thiophene). A detailed discussion of the properties will be reported in a future publication.

We are now varying the conditions in order to obtain higher quality films with higher conductivity. However, we have shown that poly(pyridazine) can be polymerized electrochemically, and that its properties are characteristic of conducting polymers such as poly(thiophene) and poly(pyrrole).

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