Modification of Growth Rate and Structure of Electropolymerised Aniline by Sodium Polyvinyl Sulphonate

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The electropolymerisation of aniline is accelerated by the presence of sodium polyvinyl sulphonate in the monomer solution and can be initiated at a less anodic potential than in its absence while the densely compact structure of the polymer is retained.

Polyaniline (PANI) can be prepared electrochemically from aqueous solutions, producing an electroactive conducting film, stable in air and water, on the anode.[1] The polymer consists of *para*-coupled aniline units growing initially in a globular structure but evolving eventually to a fibrous mat, as observed in scanning electron microscopy (SEM) images.[2] It is already well known that the polymer structure is affected by conditions employed during film preparation, such as electrical potential,[3] reactant concentration,[4] and pH.[5] Growth rate enhancement and structure modifications have also been observed for aniline copolymerisation with other substituted aromatic compounds.[6] Here we report that sodium polyvinyl sulphonate (PVSNa) also significantly modifies the growth rate and the structure of the electropolymer.

Electropolymerisation was carried out by the now well established method of cycling the potential of a platinum electrode between −0.18 and +0.78 V (*vs.* standard calomel electrode, SCE) in an acidic aqueous solution of the monomer. The cell was a single compartment 3-electrode system, with a standard SCE reference and a platinum foil counter electrode. The sequence of deposition was programmed and controlled with a Princeton Applied Research model 273 potentiostat. In Fig. 1*a*, the cyclic voltammogram of polymer growth of a 0.2 M aniline hydrochloride (Fluka) monomer solution in 1 M HCl is presented. A second similar solution was prepared, and PVSNa was added to a concentration of 520 mg (0.04 M of monomer unit) in 50 ml. The resulting cyclic voltammogram of the PANI growth is

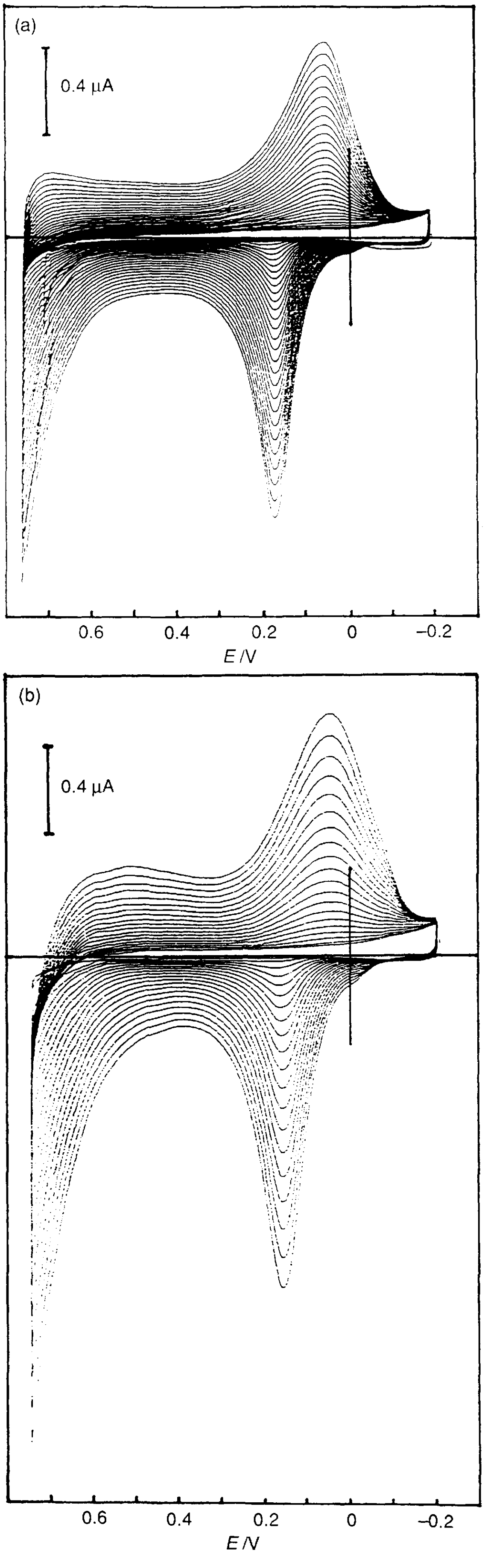

Fig. 1 Sequential cyclic voltammograms during electropolymerisation of aniline on a platinum plate in 1 M HCl solution and potential scan rate of 50 mV/s (*a*) in the absence of and (*b*) in the previous of PVSNa

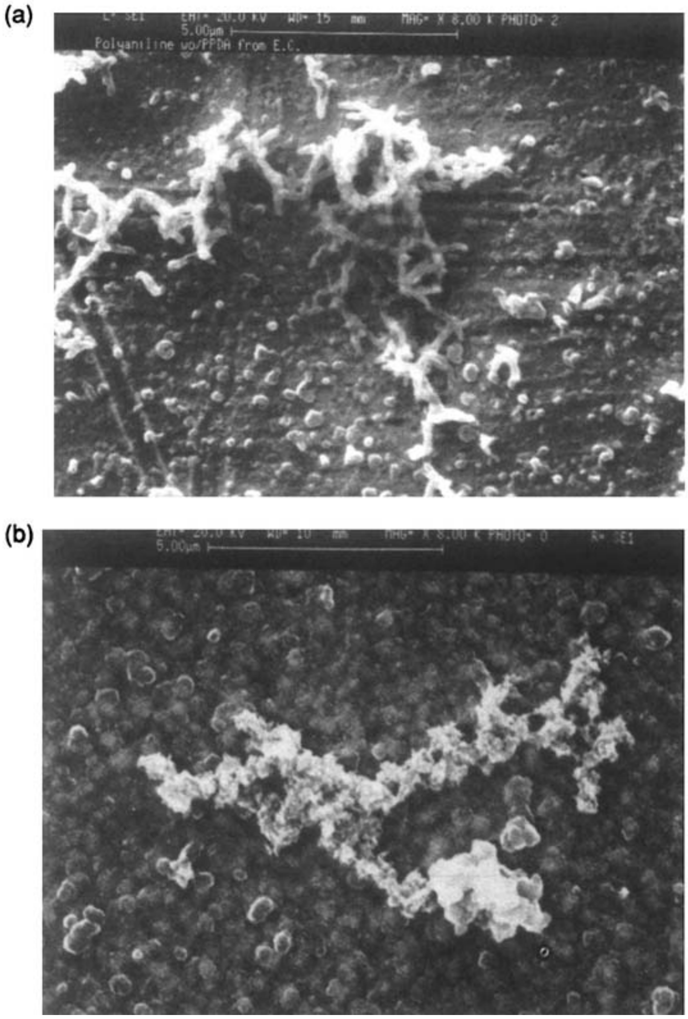

Fig. 2 SEM images of structure of PANI thick films following 30 cycles of electropolymerisation (*a*) in the absence of and (*b*) in the presence of PVSNa

shown in Fig. 1*b*. The acceleration in film growth rate is evident. When the pH of the monomer solution is raised by adding NaOH (*i.e.* in the range of pH 2 to 3), the rate difference was even more significant. However, electroactive PANI cannot be deposited for pH >4. Further increase in the PVSNa concentration enhances the polymerisation rate, but with a saturation effect at 0.01 M, or 130 mg PVSNa in 50 ml solution. These results may be related to the critical micelle concentration (CMC) of PVSNa in the electropolymerisation medium. Generally, the CMC of PVSNa is known to be quite low. Once the micelle state is formed, it can incorporate the aniline monomer to a high local concentration. In fact with PVSNa, the electropolymerisation of aniline can be observed at anodic potentials as low as 0.68 V (*vs.* SCE) at pH 0, and 0.40 V (*vs.* SCE) at pH 2.6; the underpotential is attributed to these concentration effects. Similar effects have also been recently observed with other surfactants, *e.g.* sodium dodecyl sulphate (SDS).

As already mentioned, the structure of the PANI film is also modified by the presence of PVSNa. The globular structure of the initial deposit of PANI is retained to considerable thicknesses in the presence of the surfactant. This is attributed also to micellar encapsulation of the monomer, which significantly modifies its transport to the electrode surface. The relevant structures are presented in electron micrographs (see Fig. 2).

The electroactive and redox properties of the resultant films, in contrast, are not significantly modified.

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