

Novel Colloidal Dispersions of Polyaniline

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Colloidal polyaniline¹ has been prepared in good yield (>50%) using a tailor-made random co-polymer as a steric stabiliser, which is *chemically* grafted onto the polyaniline microparticles formed by the oxidative polymerisation process.

In 1983 polyaniline was 'rediscovered' as a conducting polymer by MacDiarmid and co-workers,²⁻⁴ although its unusual transport properties had been investigated some years previously.⁵ A non-oxidative proton-doping process results in a highly environmentally stable material with a conductivity in the range 1-10 S cm⁻¹. Its chemical synthesis involves the oxidation of aniline monomer in aqueous acidic media by reagents such as ammonium persulphate or potassium dichromate.^{6,7} Although its air-stability is attractive, polyaniline suffers from poor processability, being only slightly soluble in polar solvents such as dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO).⁸

Recently the preparation of a colloidal form of another conducting polymer, polypyrrole, has been described.⁹⁻¹² In this approach, spherical sub-micronic polypyrrole particles are sterically-stabilized by the *physical* adsorption of commercially-available water-soluble polymers such as poly(vinyl alcohol-co-acetate), poly(vinyl pyrrolidone), or methyl cellulose. Such systems significantly enhance the processability of the normally intractable electroactive component. Most of our attempts to produce microscopic polyaniline particles by analogous methods have resulted in macroscopic precipitation due to inefficient adsorption of the stabilizer,¹³ although in certain cases a low yield of colloidal polyaniline has been obtained.^{14,15}

The steric stabilizer employed was poly(2-vinylpyridine-co-*p*-aminostyrene), synthesized by the free-radical copolymerization of 2-vinylpyridine and *p*-aminostyrene (both ex. Polysciences) using 2,2'-azobisisobutyronitrile in toluene at *ca* 60 °C. Gel permeation chromatography measurements indicated a number-average molecular weight of 21 500 and a polydispersity index of 2.5; the copolymer contained approxi-

mately 5.4 mol % *p*-aminostyrene as determined by ¹H n.m.r. spectroscopy.

It was envisaged that the pendant aniline moiety in the copolymer would participate in the *in situ* polymerization of aniline *via* a mechanism similar to that outlined by previous workers.⁸ However, we encountered some initial difficulty in the choice of a suitable oxidant: ammonium persulphate, sodium persulphate, ammonium dichromate, and iron(III) chloride all proved to be incompatible with the stabilizer, resulting in the formation of insoluble complexes. Very recently Pron *et al.* reported that potassium iodate could be used over a wide range of reaction conditions to produce good quality bulk polyaniline powder.¹⁶ We found that this oxidant did not cause precipitation of the stabilizer; as a consequence it became the reagent of choice for the preparation of colloidal polyaniline.

The synthesis was carried out as follows: potassium iodate (0.45 g) and stabilizer (1.00 g) were dissolved together in 100 ml of 1.2 M hydrochloric acid at room temperature. Aniline (1.0 ml) was injected into the stirred reaction mixture and allowed to react for 95 h. At the end of this period the solution had turned dark green with only trace precipitation of polyaniline being observed. This dispersion was centrifuged at 10 000 r.p.m. for 90 min, the supernatant decanted, and the dark green sediment re-dispersed in de-ionized water *via* ultrasonics. A small sample of the redispersed colloid was examined by transmission electron microscopy using a Philips EM 410 instrument. The particles had a 'rice grain' morphology, with an average length of approximately 120 nm (standard deviation ±20%) and an aspect ratio of 2.1 (see Figure 1).

A visible absorption spectrum of the diluted colloidal

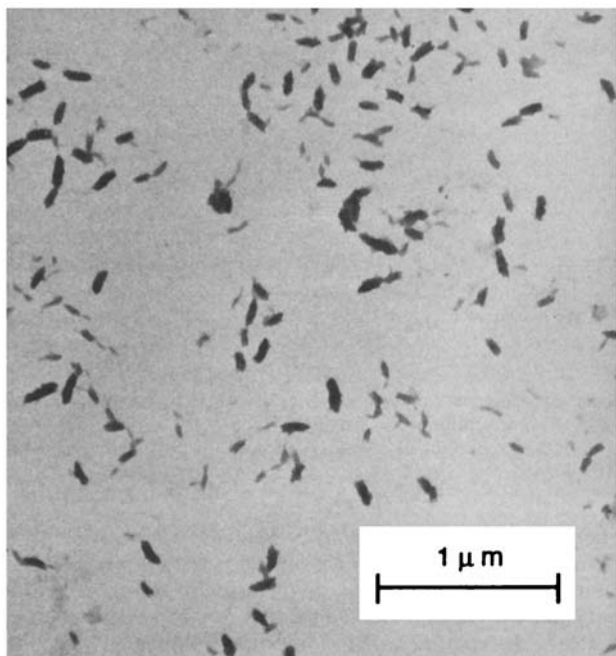


Figure 1. A representative transmission electron micrograph depicting the 'rice-grain' morphology of the colloidal polyaniline particles.

dispersion was identical to that reported by previous workers for electrochemically-synthesized polyaniline film.¹⁷ It was found that these polyaniline dispersions could be reversibly flocculated/stabilized by the addition of base/acid due to deprotonation/protonation of the outer layer of poly(2-vinylpyridine) stabilizer. We have observed similar results for polypyrrole colloids stabilized by both poly(2- and 4-vinylpyridine)-based copolymers.^{18,19}

Removal of solvent from the colloidal dispersion yielded a dark green powder, which was compressed to produce pellets for standard four-point probe conductivity measurements.

Preliminary studies indicate conductivities of the order of 0.5 S cm^{-1} for the material.

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