

## Colloidal Dispersions of Electrically-conducting, Spherical Polyaniline Particles

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To date polyaniline particles have only been prepared having a 'rice-grain' or needle-shaped morphology; we report here the first preparation, we believe, of spherical polyaniline particles.

Of all the conducting polymers, polyaniline (or its derivatives) will probably prove to be among the most useful.<sup>1</sup> It has good thermal and oxidative stability, and its conductivity is readily 'tuned' by varying the pH at which it is prepared; it is conducting at low pH and insulating at high pH. However, like most conducting polymers prepared to date, it is somewhat intractable and is only very slightly soluble in a limited range of very polar solvents, *e.g.*, dimethylformamide or dimethyl sulphoxide.<sup>2</sup> One method of overcoming the processability problem is to prepare conducting polymers in colloidal (latex) form, *i.e.*, up to  $\sim 1 \mu\text{m}$  in size; this route has been adopted by several groups, in particular, those in Bristol<sup>3-8</sup> and Los Alamos.<sup>9-11</sup> The key to preparing such conducting polymer latices is to carry out the polymerisation in the presence of a soluble polymeric 'steric-stabiliser,' which adsorbs (or even grafts) to the latex particles as they form, preventing gross aggregation and precipitation of the polymer being produced. If necessary, the stabiliser may be subsequently removed to yield stable dispersions of bare (charged stabilised) particles.<sup>6</sup> Colloidal latex particles have been shown to have electrical conductivities up to  $\sim 10 \Omega^{-1} \text{cm}^{-1}$ .

Colloidal particles prepared in this way may be further 'processed' in a variety of ways. For example, Cooper and Vincent have recently described how polypyrrole and polyaniline particles may be incorporated into thin film polymeric films by mixing them with other, film-forming latex particles, or coating them as dispersions in a film-forming polymer solution.<sup>7</sup> The same authors have also shown how such particles can be encapsulated into larger polymer beads (typically 0.05–0.5 mm diam.);<sup>12</sup> these may then be injection-moulded, *etc.*, to form bulk polymeric materials of any desired shape. Another potential use of colloidal conducting polymers is in separation processes, *e.g.*, filtration or chromatography; by applying a controlled, but variable, electrostatic potential

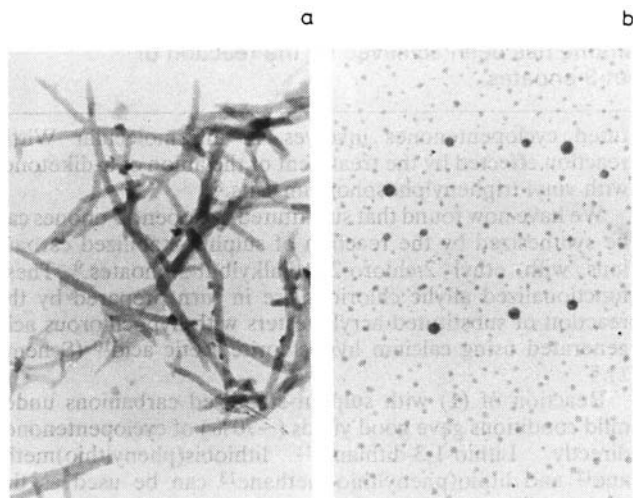
to a packed-bed of such particles, ionic species may be selectively adsorbed (and subsequently desorbed) from a flowing solution.

Clearly, in the various examples quoted, control of the particle morphology is very desirable. In the case of the thin polymeric films, for example, the use of rod or needle-like particles ensures that electrical conductivity is maintained, at relatively low volume fractions of the conducting particles, by a percolation mechanism.<sup>7</sup> On the other hand, in the case of chromatographic beads, spherical particles would be more desirable.

To date the two main conducting latex particles studied have been polypyrrole<sup>4-6,9</sup> and polyaniline.<sup>7,10,11</sup> Polypyrrole can be readily prepared as spherical particles,<sup>4</sup> whereas polyaniline has only been prepared with 'rice-grain' or needle-shaped particles.<sup>7,10</sup> Some earlier studies by Edwards *et al.*,<sup>3</sup> in this laboratory, on the formation of polyacetylene particulate dispersions gives the main clue as to what is happening. Dispersions of colloidal particles will often tend to aggregate in chain-like structures, to minimise the hydrodynamic repulsion between approaching particles. This situation is enhanced if there also exists long-range electrostatic repulsion between the particles, *e.g.*, in aqueous dispersions where the particle surfaces are charged. Moreover, if the attractive (van der Waals) forces holding the particles in contact are strong enough, then re-orientation of the particles in an aggregate is unlikely. Hence, the common form of aggregate structure in such systems is a cross-linked mesh of particle chains. This accounts for the gel-like structure normally observed, for example, in polyacetylene prepared and precipitated in solution. Recently, Armes *et al.*<sup>13</sup> have shown, using scanning-tunnelling microscopy, in the case of polyaniline, that the needle or rice-grain shaped particles, produced in a typical sterically-stabilised, dispersion-polymerisation of aniline, do indeed consist of much smaller spherical particles.

The key therefore to producing individual spherical particles must be more efficient steric stabilisation during the early stages of the dispersion polymerisation process. This means using polymers which adsorb very rapidly onto the emerging particles compared to the rate of growth and the diffusion rate of the particles themselves.

We have shown that for polyaniline prepared in aqueous hydrochloric acid solution ( $1.2 \text{ mol cm}^{-2}$ ), using potassium or ammonium persulphate as oxidant (at an oxidant:aniline mole ratio of 0.19:1), the choice of stabiliser was critical in controlling the type of particle morphology that resulted.<sup>7</sup> Stable dispersions of polyaniline could be prepared using homopolymer poly(ethylene oxide) (PEO) ( $M > \sim 10^5$ ), but only long needle-shaped particles resulted, Figure 1(a).† Lower  $M$  PEO fractions would adsorb faster, but they only adsorb weakly and reversibly, rendering steric stabilisation ineffective. In order to overcome this problem, PEO chains, with  $M$  2000, but end-capped with an acrylate group (which



**Figure 1.** (a) Needle-shaped polyaniline particles produced using poly(ethylene oxide),  $M$  300000, as stabiliser<sup>7</sup> (magnification:  $\times 32000$ ). (b) Spherical polyaniline particles produced using graft copolymer described in text as stabiliser (magnification:  $\times 10000$ )

† Aggregates in the electron micrograph shown are thought to be an artefact; they are probably formed on 'drying' the dispersion on the electron microscope grid.

can co-polymerise into the growing polyaniline chains) were used; the stabiliser chains are then effectively grafted to the polyaniline latex particles. However, needle-shaped particles again resulted; this is probably because the steric-stabiliser sheath around the particles is too thin to give efficient steric-stabilisation (*i.e.*, to oppose the strong van der Waals forces between polyaniline particles).

We found that needle-shaped particles, with much shorter axial ratios (*i.e.*, rice-grains), could be prepared using more effective steric-stabilisers, namely graft-copolymers, having an ethylacrylate/styrene/linear copolymer backbone, with pendant (PEO) side-chains. Armes and Aldissi<sup>10</sup> have also shown that rice-grains can be formed if a random copolymer of 2-vinylpyridene/aminostyrene, or of vinylalcohol/vinyl acetate, derivatised with pendant aniline groups, is used in the polymerisation of aniline. In this case it has been shown that the aminostyrene or aniline groups, respectively, become co-polymerised in the growing polyaniline chains, again leading to effective grafting of the stabiliser to the particles.

We believe that even more efficient steric stabilisation could be achieved if a graft copolymer is used (rather than a random copolymer), but one in which the backbone is now grafted to the surface, *e.g.*, with an acrylate backbone containing pendant polymerisable groups (*e.g.*, glycidyl groups), as well as the pendant PEO chains. Such a polymer was kindly supplied to us by ICI Paints Division plc, Slough, Berkshire, UK. Using this polymer as the stabiliser at a concentration of 2.8 wt% in solution, we found that we could prepare spherical particles, Figure 1(b), even though these were rather poly-dispersed in size. The conductivity of the particles was found, using the usual four-point probe method, to be 3–4  $\Omega^{-1} \text{ cm}^{-1}$ .

We found that the conductivity of the polyaniline particles fell, approximately linearly, with pH, from the above value at pH ~1 (where the aqueous dispersions were green) to ~0‡ at pH ~10 (where the aqueous dispersions were blue). Control of particle conductivity in this way could clearly be a desirable asset in various applications.

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‡ *I.e.*, smaller than could be determined within the sensitivity limits of the four-point probe apparatus used.