

Dispersions of Electrically Conducting Polypyrrole Particles in Aqueous Media

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Conducting polypyrrole particles in the size range 50–250 nm diameter have been prepared by a dispersion polymerisation route in aqueous media using $\text{Fe}^{\text{III}}\text{Cl}_3$ as the initiator-dopant.

Original syntheses of doped, conducting polypyrrole used electrochemical methods.¹ Recently, however, it has been shown that chemically synthesised polypyrrole exhibiting comparable conductivities can be prepared by the polymerisation of pyrrole by various oxidants in both aqueous and non-aqueous media.^{2,3} The polymer precipitates from solution, and therefore, in principle, the presence of a suitable steric-stabiliser should lead to particle formation by the established dispersion polymerisation mechanism.⁴ Edwards *et al.*⁵ showed that latex forms of other conducting polymers could be prepared by this method. In this communication we report the formation of colloidal polypyrrole particles. Very recently,⁶ similar findings were published by Bjorklund and Liedberg. However, we believe that our method leads to better control over particle morphology and, furthermore, that their suggested charge stabilisation mechanism is incorrect.

In our experiments the following general method of preparation was used. To a stirred, aqueous solution of anhydrous FeCl_3 and a water-soluble polymer, pyrrole (or a solution of pyrrole in ethanol) was added at room temperature. The characteristic brown-black colour of doped polypyrrole developed within a few minutes. Stirring was maintained for a period of at least 16 h, without any evidence of macroscopic precipitation of polymer. Centrifugation (at 15 000 r.p.m. for *ca.* 60 min), however, led to a compact, brown-black sediment, which was readily redispersed in water after removal of the (generally clear) supernatant liquid. A typical transmission electron micrograph of the redispersed particles is shown in Figure 1. These redispersed particles were freeze-dried from water and subsequently compressed into pellets to enable bulk conductivity measurements to be made using a standard four-point probe technique.

The water-soluble polymer present during the polymerisation clearly acts as a steric-stabiliser. Even though the stabiliser may complex with the $\text{Fe}^{\text{III}}\text{Cl}_3$ (see later) to form a pseudo-polyelectrolyte, it is extremely unlikely that electrostatic repulsion plays any part in maintaining particle stability at the ionic strengths present in the aqueous phase ($>0.1 \text{ mol dm}^{-3}$), as suggested by Bjorklund and Liedberg.⁶ In their system the rôle played by the methylcellulose was 'not clear';

we believe that it similarly acts as a steric-stabiliser and its presence is a prerequisite for particle formation.

Of a wide variety of potential polymeric steric-stabilisers, only two were found to be effective: poly(vinylpyrrolidone) (PVP; $M \geq 40\,000$) and poly(vinyl alcohol-co-acetate) (PVA; 88 or 96% alcohol; $M \geq 95\,000$). Poly(ethylene oxide), poly(acrylic acid), and various block copolymers based on poly(ethylene oxide) all failed to provide effective steric stabilisation. It is of interest to note that Hirai *et al.*⁷ showed that PVA, PVP, and various cellulose derivatives were also effective in stabilising aqueous colloidal dispersions of copper particles. The concept of steric stabilisation was also invoked by these workers to explain particle formation.

Of the two polymers, PVA, in general, led to more monodisperse particles and required a lower ratio of stabiliser to monomer for successful particle formation. The average size of the polypyrrole particles decreased with increasing stabiliser to monomer ratio.

The rate of addition of the pyrrole monomer also appears to affect the particle size; slower feed-rate leads to the formation of larger particles. The order of addition of the reactants is important; for example, the addition of an aqueous solution of initiator to a stirred solution of pyrrole monomer plus stabiliser led to non-spherical particles. By varying the concentrations of the reactants over a reasonable range, particles having mean diameters in the range 50 to 250 nm could be prepared. Full details will be published elsewhere.

Although varying the water : ethanol solvent ratio did not lead to any systematic trends in particle size variation, the highest electrical conductivity ($\sim 1.5 \Omega^{-1} \text{ cm}^{-1}$) was obtained in the *absence* of ethanol. This value is nearly an order of magnitude higher than the value quoted by Bjorklund and Liedberg⁶ for their polypyrrole particles. The actual values obtained, resulting from bulk measurements on compressed pellets, will, of course, depend on how much and what type of stabiliser polymer is present in the pellets. Preliminary measurements suggest that the mass ratio for the case of the PVA-stabiliser particles is $\sim 0.12 : 1.00$ stabiliser : polypyrrole.

Visible absorption spectroscopy of aqueous dispersions of the polypyrrole latices gave a peak at 460 nm and gradually increasing absorbance above 600 nm. A Fourier-transform i.r.

spectrum of the polypyrrole particles dispersed in a KBr pellet was very similar to that reported for doped polypyrrole perchlorate films prepared by an electrochemical synthesis.⁸

The concept of pre-reaction complexation between monomer and initiator in the chemical synthesis of macroscopic polypyrrole in organic media has already been postulated.³ However, our latex system appears to be rather more complicated with complexation possible between both monomer and stabiliser⁹ and initiator and stabiliser.^{10,11} Since, during our synthesis, the pyrrole monomer is rapidly polymerised on addition to an initiator-stabiliser mixture, we believe that the latter is more likely to be important with regard to particle formation.

A preliminary equilibrium dialysis experiment with an aqueous solution of PVP 700 000 and an equimolar amount of anhydrous FeCl_3 (with respect to the pyrrolidone sub-unit) confirms pre-reaction complexation. Analysis for Fe by atomic absorption spectroscopy indicates an empirical formula of $[\text{Fe}(\text{C}_6\text{H}_9\text{NO})_{3.5}]$ for the complex. Fourier-transform i.r. spectroscopy indicates that the iron species is complexed to the oxygen atom of the pyrrolidone sub-unit since a spectral shift to lower wavenumber was observed for the C=O bond.

Initially it was considered that at least part of the observed shift might be due to protonation of the C=O bond, given the high acidity ($\text{pH} \leq 1$) of the aqueous Fe^{III} solution. However, careful control experiments have ruled out this possibility: the shift is *entirely* due to complexation.

The observed shift and empirical formula is similar to that reported by other workers for analogous complexes.¹¹

Although further experiments are necessary to examine the Fe^{III} -PVA system, it is likely that complexation occurs in an analogous manner between the Fe^{III} species and the acetyl groups in PVA. We have found in accordance with other workers that microanalysis of macroscopic polypyrrole formed in the absence of stabiliser shows the absence of iron. However, microanalysis of the latex powder indicates the presence of both stabiliser and iron; this is further evidence for complexation between the iron(III) species and the stabiliser. It is possible that the pseudo-polyelectrolyte resulting from this complexation leads to an increase in the anchoring efficiency of the stabiliser on the polypyrrole particles. It is interesting to note that, for the case of the addition of the initiator to the stirred monomer-stabiliser mixture, non-spherical particles of poor morphology were obtained. This is

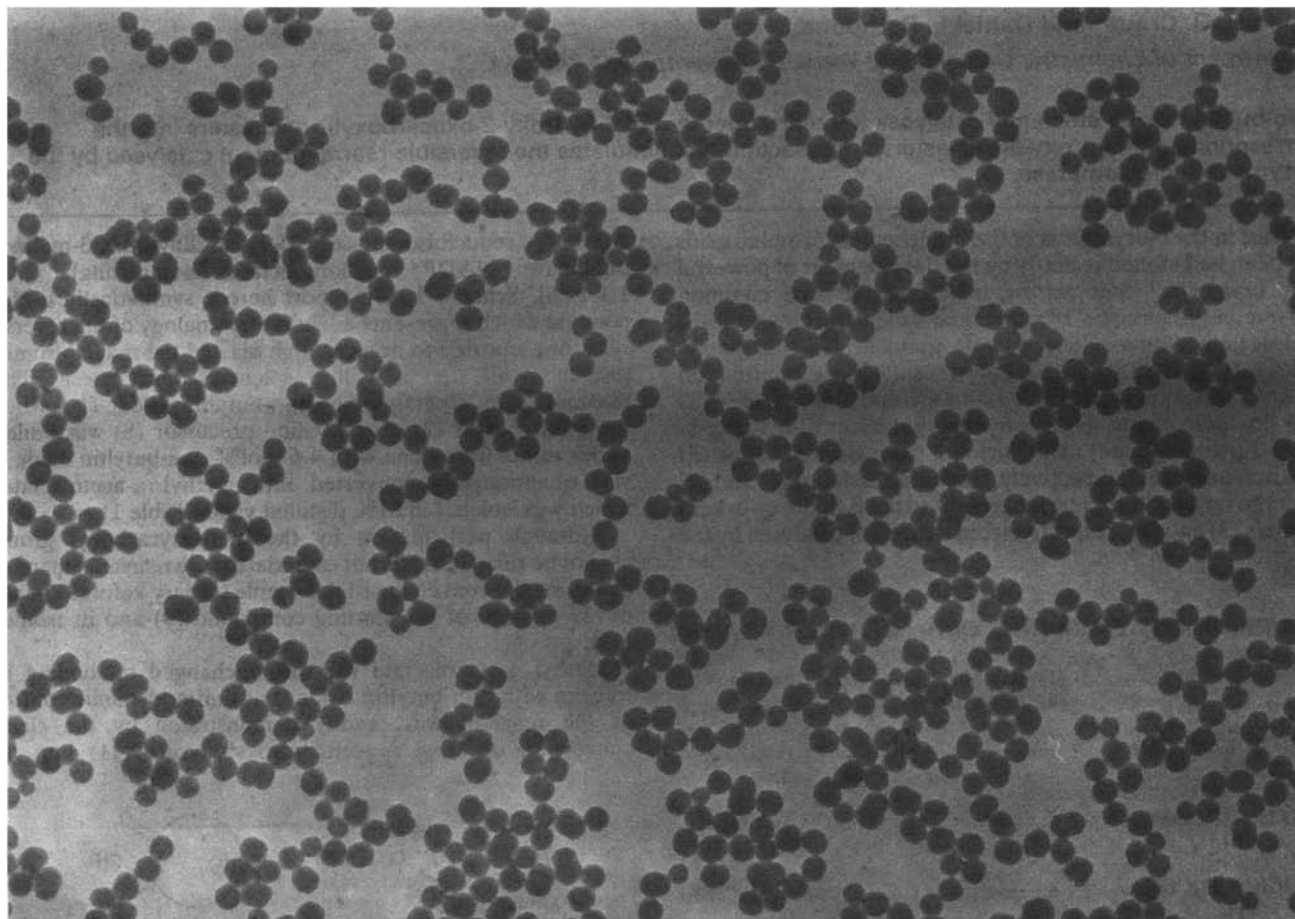


Figure 1. Polypyrrole latex particles: magnification 20 000; average diameter ~ 75 nm; steric-stabiliser PVA (88%; M 125 000).

further, albeit indirect, evidence for the importance of the pre-reaction between initiator and stabiliser in promoting uniform latex particle formation.

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