Colloidal Dispersions of Electrically Conducting Polypyrrole Particles in Various Media

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Stable colloidal dispersions of polypyrrole latex particles in water and methanol (charge-stabilised), and in dioxane (sterically stabilised) have been prepared; the particles have a conductivity of *ca.* 1—2 S cm^{-1}.

In recent publications[1,2] we showed how sterically stabilised dispersions of electrically conducting polypyrrole (PPy) particles in water may be prepared by the dispersion polymerisation of pyrrole monomer in aqueous (or aqueous ethanolic) media, using $FeCl_3.6H_2O$ as the initiator, and a polymeric stabiliser for the emergent PPy particles. In these studies the stabilisers used were either poly(vinylpyrrolidone) (PVP) or partially hydrolysed poly(vinyl acetate) (PVA). The particles (with their adsorbed polymer layer) were dialysed against water, freeze-dried, and pelletized. The conductivity of the pellets decreased with increasing adsorbed amount of polymeric stabiliser. However, a minimum quantity of stabiliser is necessary to provide effective steric stabilisation of the emergent PPy particles during polymerisation in the high ionic strength aqueous medium (typically 2 mol dm^{-3}).

In order to produce conducting PPy particles which may be of interest in various applications (*e.g.* conducting composites, selective extractive technologies), it would clearly be useful to produce (charge-stabilised) dispersions of the *bare* particles; this is only possible for media of high dielectric constant (*e.g.* water, methanol) where interfacial charge may be sustained. For low dielectric constant media *steric* stabilisation remains a prerequisite. Nevertheless, by 'stripping' the PPy latex particles of their initial stabilising polymer sheath, the particles may be subsequently redispersed in the medium of low dielectric constant required, using the stabiliser of choice (*e.g.* one compatible with the matrix solid in a composite).

In one of the earlier papers[1] we stated that poly(ethylene oxide) (PEO) is not an effective stabiliser. However, only PEO samples of molecular weight (M) $<10^5$ were investigated. We have now found that, using PEO samples of higher molecular weight, stable PPy dispersions may be prepared using the route described previously.[1,2] However, the average diameter ($\bar{d}$) of the (spherical) particles produced is significantly greater than those produced using either PVP or PVA as the stabilising polymers. With the latter stabiliser $\bar{d}$ is typically in the range 70—150 nm, whereas with PEO the following sizes were obtained: PEO M 3 × 10^5, $\bar{d}$ 445 ± 45 nm; PEO M 4 × 10^6, $\bar{d}$ 350 ± 40 nm.† Clearly these data reflect the much weaker adsorption affinity of PEO on PPy surfaces. With PVP or PVA there may well be H-bonding between the N–H of the pyrrole moieties in the particle surface and the C=O of the pyrrolidone or acetate moieties of the stabiliser

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† Much *smaller* particles ($\bar{d}$ *ca.* 30 nm) may be prepared using potassium persulphate as initiator, instead of $FeCl_3.6H_2O$.

chains;[2] any similar interaction between the pyrrole N–H groups and the ether oxygen in the PEO chains is expected to be much weaker.

The production of the *bare* PPy particles already referred to was readily achieved by several (typically >5) centrifugation/redispersal in pure water cycles for the PPy latex particles. Elemental analysis of the latex particles was used to check that the PEO chains had been successfully 'stripped' from the surfaces after the necessary number of centrifugation/redispersal cycles.

Further (indirect) evidence that the particles were now 'bare', and hence purely charge-stabilised, was provided by the facts that: (a) the aqueous PPy latex rapidly coagulated on addition of $MgSO_4$ solution (net concentration 0.05 mol dm^{-3}), whereas the original PEO-stabilised PPy latex particles were totally stable in this environment; (b) the bare latex particles would adsorb other water-soluble polymers (*e.g.* PVP) or polyelectrolytes [*e.g.* sodium poly(styrene sulphonate) (NaPSS)], whereas the PEO-covered particles would not. An interesting observation in this regard was that at pH 1.6, the plateau adsorbed amount for NaPSS (*M* 780 000) was *ca.* 3 mg m^{-2}, whereas at high pH (*ca.* 11) none was adsorbed. Moreover, the NaPSS adsorbed originally at pH 1.6 could be completely *desorbed* by raising the medium pH to *ca.* 11.

The electrophoretic mobility of the bare latex particles in aqueous 10^{-2} mol dm^{-3} KCl solution was measured as a function of pH; an isoelectric point at *ca.* 3 pH units was observed. These results may possibly reflect removal, with increasing medium pH, of Fe^{3+} ions complexed to pyrrole moieties at the latex particle surface. However, previous elemental analysis[1] of *macroscopic* polypyrrole, polymerised in the *absence* of stabiliser, showed no evidence of Fe^{3+} being present. It might be, on the other hand, that some Fe^{3+} ions complex with the PEO stabiliser. A more likely explanation for the mobility behaviour as a function of pH is deprotonation of the N–H groups of the surface pyrrole moieties at the particle surface. Further details of the electrophoretic mobility behaviour of the PPy latex particles will be published elsewhere.[3]

The PPy latex particles in water (relative permittivity 80) could be redispersed in methanol (relative permittivity 33) again using several centrifugation/redispersion cycles. However, the PPy particles could not be redispersed in pure solvents of low relative permittivity, *e.g.* dioxane (2), but could be redispersed from methanol into dioxane, containing dissolved (dry) high molecular weight PEO; stable dispersions result.

Pellets, for conductivity measurements, were prepared from freeze-dried PPy latex particles, in each solvent, using a Research and Industrial Co. H301 pelletizing press at 250 atm. Unfortunately, 'good' quality pellets could be obtained only when the particles were coated with the adsorbed PEO layer, *i.e.* originally in water and subsequently in dioxane. The conductivity of the pellets produced from each of these two solvents was approximately the same (*ca.* 1—2 S cm^{-1}), indicating that the intrinsic conductivity of the *particles* had not been altered by the various solvent changes. However, as has been shown,[2] the conductivity of the pellets is lowered by the presence of the adsorbed stabiliser sheath. From that point of view, it would have been of interest to measure the conductivity of the pellets produced from the *bare* latex particles. However, these were brittle and scanning electron microscopy indicated voids; hence conductivity data are unreliable. Nevertheless, the aim of producing charge-stabilised colloidal dispersions of conducting polypyrrole particles in water and methanol, and similar sterically stabilised dispersions in dioxane has been achieved. It should be straightforward to extend these procedures to other solvents; this extension could include monomers, in order to form electrically conducting composites by polymerisation of the continuous phase.

We thank Biosyn-R, Philadelphia, for financial support.

Received, 11th May 1988; Com. 8/01861H

References

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