Synthesis and characterization of micrometre-sized, polypyrrole-coated polystyrene latexes†

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Near-monodisperse, micrometre-sized poly(*N*-vinylpyrrolidone)-stabilized polystyrene latexes have been coated with polypyrrole by *in situ* deposition of the conducting polymer from aqueous solution. If the conducting polymer overlayer is sufficiently thin, it lies inside the steric stabilizer layer and the coated latexes retain reasonable colloid stability. The polypyrrole loading on the latex particles was systemically varied over a wide range (1–50 mass%) simply by changing the initial latex concentration. Pressed pellet conductivity measurements on the dried composites indicated an anomalously low percolation threshold of 1–2 vol. %, which is consistent with the conducting polymer component lying on the surface of (rather than within the interior of) the latex particles. IR spectroscopy studies of the composites confirmed the presence of several strong absorption bands due to the polypyrrole component. However, scanning electron microscopy (SEM) studies showed no evidence for the polypyrrole overlayer, which suggests that it must be very smooth and uniform. Disk centrifuge photosedimentometry (DCP) studies on the coated latexes revealed the presence of doublets and higher aggregates which indicates that these dispersions are weakly flocculated. However, if the polypyrrole overlayer is very thin (<10 nm) the coated particles exist in solution mainly as singlets with relatively few doublets or larger floccs. Polystyrene latex can also be coated with other conducting polymers such as polyaniline and poly(3,4-ethylenedioxythiophene). Finally, both polyelectrolytes and physically adsorbed poly(*N*-vinylpyrrolidone) can provide an effective steric barrier to allow controlled deposition of the conducting polymer overlayer.

Polypyrrole is a relatively air-stable organic conducting polymer which suffers from limited processability.[1] In its doped, conductive form it is usually insoluble in all organic solvents, probably due to some degree of cross-linking.[2]‡ In order to improve this material's poor processability various groups have reported the synthesis of colloidal dispersions of polypyrrole particles.[3–6] Such particles are easily prepared by carrying out the chemical polymerization of pyrrole in the presence of a suitable water-soluble polymer such as methyl cellulose or poly(vinyl alcohol). The water-soluble polymer adsorbs onto the precipitating polypyrrole nuclei and prevents further aggregation *via* a steric stabilization mechanism.[7] Thus the 'core' of these particles contains the conducting polymer, which is surrounded by an outer layer of adsorbed, solvated water-soluble polymer.

Several groups have reported using inorganic oxide dispersions as colloidal substrates for the deposition of conducting polymers. For example, Partch *et al.* have shown that colloidal inorganic oxide particles containing transition metal oxidants such as Fe^{3+} or Ce^{4+} can act as particulate oxidants for the polymerization of pyrrole monomer at elevated temperatures.[8] However, these composite particles are not normally colloidally stable unless a water-soluble polymer such as poly(vinyl alcohol) or poly(*N*-vinylpyrrolidone) is added to provide a steric barrier to particle aggregation.[9] Similarly, Armes *et al.* have chemically polymerized pyrrole (and aniline) in the presence of micrometre-sized silica particles using soluble oxidants: conducting polymer–silica composites were obtained as macroscopic precipitates.[10] Scanning electron microscopy (SEM) studies confirmed that the conducting polymer component had a globular morphology and that its deposition was inhomogeneous: some silica particles were thickly coated with conducting polymer while others remained substantially uncoated.

With regard to conducting polymer deposition onto latex substrates, Garnier's group have described the synthesis of polypyrrole-coated polystyrene latexes of sub-micrometre dimensions[11] whilst Yamamoto and co-workers reported coating styrene–butadiene latexes with polypyrrole using the H_2O_2–HBr–Fe^{3+} oxidant system.[12] In both cases the authors suggested that the presence of acidic surface functional groups (sulfonic or carboxylic acids) were important for successful composite formation. Both groups claimed that their composite particles were colloidally stable but no experimental evidence was provided in either case to support these claims. At Sussex we have spent considerable time and effort[13] attempting to repeat these syntheses using the identical latex substrates (same manufacturer, particle size, surface charge, *etc.*) described by the French and Japanese groups. Invariably we observed significant flocculation/precipitation of the composite particles: these observations are consistent with the relatively high Hamaker constant reported for polypyrrole by Vincent's group.[14] It seems, at the very least, that these syntheses are not particularly robust with respect to the colloid stability of the latex composite particles.[15] Indeed, Beadle *et al.* have shown that the chemical polymerization of aniline in the presence of chlorinated copolymer latex particles always led to the macroscopic precipitation of the polyaniline–copolymer latex composites.[16] In this latter study the conducting polymer loading in the composite was conveniently controlled by varying the initial copolymer latex concentration at a fixed concentration of aniline monomer and oxidant.

In 1993 Yoshino *et al.* reported the deposition of a thin (10–20 nm) polypyrrole overlayer onto 10 μm diameter polyethylene spheres.[17] These coated particles were then mixed with the original uncoated polyethylene spheres and hot-pressed at 90–130 °C to form semiconductive composites. These composites exhibited very low percolation thresholds at polypyrrole loadings of 0.1–0.2 vol.%. However, the Japanese group's study emphasized the electrical properties of the hot-pressed composite materials and potential applications; the polypyrrole-coated polyethylene particles themselves were not extensively characterized. For example, no attempt was made to examine the morphology of the polypyrrole overlayer by

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‡ Very recently a Korean group have reported that, under carefully controlled synthesis conditions, it is possible to obtain non-cross-linked polypyrrole chains which can be rendered soluble in *m*-cresol using surfactant-type dopant anions.

electron microscopy and no spectroscopic studies were reported.

Recently Wiersma *et al.* at DSM Research have demonstrated that submicrometre-sized sterically stabilized latex particles can be coated with polypyrrole (or polyaniline) in aqueous media to form conducting polymer composite latexes with good colloid stability.[18] These workers emphasise that using an adsorbed non-ionic polymeric stabilizer such as poly(ethylene oxide) or hydroxymethylcellulose in these syntheses is critical for producing stable colloidal dispersions at high Fe^{3+} concentrations: all control experiments carried out in the absence of such non-ionic stabilizers resulted in macroscopic precipitation.[18a] Transmission electron microscopy (TEM) studies on the coated particles provided direct evidence for a 'core–shell' morphology and both aqueous electrophoresis and dielectric measurements supported this observation.[18b] It was suggested that the conducting polymer is formed as a thin layer at the surface of the latex particles without significantly interfering with the steric stabilization mechanism conferred by the solvated outer layer of non-ionic polymer (see Fig. 1). The Dutch group have focused on coating low T_g latexes of 50–500 nm diameter based on polyurethane, poly(vinyl acetate) or alkyd resins.§ Unlike the sterically-stabilized polypyrrole dispersions described above, such composite particles exhibit remarkably good film formation properties at room temperature, despite encapsulation of the low T_g latex component by an outer layer of high T_g conducting polymer. Solid-state conductivities were reported to lie in the range 10^{-5}–10^{1} S cm^{-1}, depending on the conducting polymer loading. However, there is some evidence that the coating process may be somewhat inhomogeneous and/or inefficient: depending on the reaction conditions, a substantial fraction of the latex substrate can remain uncoated.[19]

In a recent communication[20] we reported that the DSM coating protocol can be easily adapted in order to coat micrometre-sized, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex particles with a polypyrrole overlayer (see Fig. 1). Polystyrene was selected as a 'model' substrate since it has a relatively high T_g (rigid, non-deformable particles) and latexes can be readily synthesized with narrow size distributions over a wide size range (50 nm–10 μm).[21,22] Potential applications for these micrometre-sized coated latexes include an improved stationary phase for electrochromatography[23] and novel 'marker' particles for visual agglutination diagnostic assays.[24] In the present study we describe our preliminary findings in more detail and include our latest results.

Experimental

Materials

Styrene (Aldrich) was purified by passing through a column of activated neutral alumina to remove the inhibitor. Two grades of poly(*N*-vinylpyrrolidone) (PVP), with molecular masses of 44 000 and 360 000 respectively, were obtained from BDH and used without further purification. Aliquat 336 (Aldrich) and azoisobutyronitrile (BDH) were used as supplied. Pyrrole was kindly donated by BASF; it was purified by passing through a column of activated basic alumina and stored at −15 °C prior to use. $FeCl_3 \cdot 6H_2O$, $(NH_4)_2S_2O_8$, H_2O_2 (27.5 mass% soln.) and HBr (48% soln.) were all purchased from Aldrich and used without further purification.

Polystyrene latex synthesis

The PVP steric stabilizer (7.5 g) and tricaprylylmethylammonium chloride (Aliquat 336; $MeN[(CH_2)_7Me]_3Cl$) surfactant co-stabilizer (2.0 g) were dissolved in isopropyl alcohol (400 ml) in a 1 l round-bottomed flask fitted with a condenser and a magnetic stirrer bar. After heating to 70 °C under a nitrogen blanket, the reaction vessel was purged with a stream of nitrogen for 1 h at 70 °C. Then a solution of azoisobutyronitrile initiator (0.50 g) predissolved in styrene monomer (50 g) was added to the reaction vessel with vigorous stirring. The styrene polymerization was then allowed to proceed for 24 h before cooling to room temperature. The resulting latex particles were then purified by repeated centrifugation–redispersion cycles (replacing successive supernatants with deionized water). The latex syntheses were carried out three times under the above conditions (or similar) using PVP stabilizers having molecular masses of either 44 000 or 360 000.

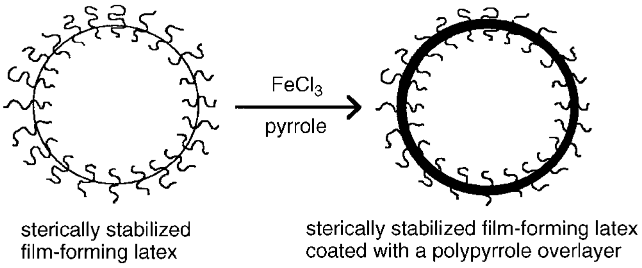

Fig. 1 Schematic formation of polypyrrole-coated latex particles. Note that the deposited conducting polymer overlayer lies inside the solvated steric stabilizer layer.

Polystyrene latex characterization

The latexes were sized using disk centrifuge photosedimentometry (DCP). All measurements were carried out using a Brookhaven BI-DCP instrument, operating in the line start mode. Samples for DCP analysis were prepared by adding a few drops of the aqueous latex mixture to 3 ml of a 1 : 2 v/v% methanol–water mixture. This solution was immersed in an ultrasonics bath for 1–10 min just prior to DCP analysis. The centrifugation rate was adjusted to between 2000 and 3000 rpm, depending on the size of the particles being measured. A particle density of 1.05 g cm^{-3} was assumed for the polystyrene latex particles.¶ DCP confirmed that the three latexes had relatively narrow size distributions, yielding mass-average particle diameters of 1.57 ± 0.12, 1.80 ± 0.06 and 1.64 ± 0.03 μm. These sizes were confirmed by TEM (Hitachi 7100 instrument) and SEM studies (Leica Stereoscan 420 instrument) on gold-coated dried latexes. One of the latexes was analyzed by FTIR spectroscopy (KBr disk) using a Nicolet Magna Series II spectrometer (64 scans, 4 cm^{-1} resolution).

Polypyrrole coating protocol

PVP-stabilized polystyrene latexes. $FeCl_3 \cdot 6H_2O$ oxidant (0.91 g) was dissolved into an aqueous solution of the PVP-stabilized polystyrene latex (0.10–12.40 g dry mass), in a screw-cap bottle with magnetic stirring. Pyrrole (0.10 ml) was added *via* a syringe and the polymerization was allowed to proceed for 24 h. The coated latex particles were then purified by repeated centrifugation–redispersion cycles (successive supernatants being replaced by deionized water) in order to remove the inorganic by-products of the pyrrole polymerization. CHN elemental microanalyses were determined for each oven-dried coated latex. The polypyrrole loadings of each of the coated

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§ DSM Research are currently marketing a commercial latex for antistatic and anticorrosion applications under the tradename ConQuest.

¶ The DCP technique is seldom applied to sterically stabilized latex particles because the solvated stabilizer layer leads to considerable uncertainty in their effective particle density, which is an important input parameter for DCP. However, for the micrometre-sized latexes studied here, the stabilizer layer *d* is so thin relative to the particle diameter *D* (typically *d* is 10–20 nm and *D* is at least 1570 nm) that this potential source of error was considered to be negligible. Indeed, excellent agreement was always obtained between the DCP data and our electron microscopy studies.

latexes were determined by comparing their nitrogen contents to that of the corresponding uncoated polystyrene latex (N *ca.* 0.17–0.21%), and conventional polypyrrole 'bulk powder' (N = 16.5 ± 0.5%) synthesized in the absence of any latex particles. Polystyrene latexes were also coated with polypyrrole using two alternative oxidant systems: $(NH_4)_2S_2O_8$ (0.38 g) and H_2O_2 (0.20 ml, 27.5% soln.). With the latter oxidant system both HBr (0.30 ml, 48% soln.) and a catalytic amount of $FeCl_3$ were added, as described by Yamamoto and co-workers.[12,25] Finally, in some experiments the polystyrene latexes were coated with thin overlayers of either polyaniline or poly(3,4-ethylenedioxythiophene) using $(NH_4)_2S_2O_8$ or $Ce(SO_4)_2$ respectively.

Charge-stabilized polystyrene latex. The procedure for coating the 1 μm diameter charge-stabilized polystyrene latex (kindly donated by Polymer Laboratories, UK) was essentially the same as that described for the sterically stabilized polystyrene latexes, except that PVP was physically absorbed onto the latex prior to the addition of the oxidant. The PVP was present in significant excess to ensure complete coverage of the charge-stabilized latex. Thus, PVP (94.6 mg, M_W 44 000) was dissolved in 5.85 g of an aqueous dispersion of the latex (10 mass% solids content). This reaction solution was then stirred for 24 h prior to addition of the $FeCl_3$ oxidant (0.566 g), followed by injecting the pyrrole monomer (62.5 μl) *via* a micropipette. Latex clean-up was carried out as described earlier. As a control experiment, deposition of polypyrrole onto the charge-stabilized polystyrene latex particles was also attempted in the absence of PVP.

Other steric stabilizers. A polystyrene latex of 670 nm diameter was synthesized in alcoholic media using a poly[(2-dimethylamino)ethyl methacrylate–block–methyl methacrylate] (PDMAEMA–PMMA) copolymer stabilizer as described previously.[26] The PMMA block acts as an anchor and adsorbs onto the surface of the polystyrene particles while the PDMAEMA block acts as the solvated stabilizer layer. After centrifugation clean-up, this latex was coated with polypyrrole using an $FeCl_3$ oxidant in 1.2 M HCl. Since the PDMAEMA block is highly protonated in this acidic solution this steric stabilizer behaves as a cationic polyelectrolyte during the pyrrole polymerization.

Characterization of the polypyrrole-coated polystyrene latexes

Chemical composition. FTIR spectra of latex composites dispersed in KBr disks were recorded using the instrument described above. After clean-up, all uncoated and coated latexes were oven-dried overnight at 60 °C prior to CHN elemental microanalyses at an independent laboratory (Medac Ltd at Brunel University, UK).

Particle size analysis and degree of dispersion. Disk centrifuge studies were carried out as described earlier. It was assumed that the polypyrrole-coated polystyrene latexes had the same scattering characteristics as carbon black. The densities of the dried composite latexes were determined using helium pycnometry (Accupyc 1330, Micromeritics).

Conductivity and conductivity stability measurements. The conductivities (σ) of compressed pellets of the polypyrrole-coated polystyrene latexes were determined using standard four-point probe techniques at room temperature. These measurements were repeated at regular intervals over a period of several months. Random errors associated with these measurements are estimated to be approximately 10%, with an additional systematic error of *ca.* 5–10%.

Results and Discussion

Three poly(*N*-vinylpyrrolidone)-stabilized polystyrene latexes were synthesized according to protocols described in the literature.[21,22] Disk centrifuge and electron microscopy studies confirmed that these three latexes were in the micrometre size range and that each latex had a reasonably narrow size distribution. A typical TEM of one of the latexes is shown in Fig. 2. FTIR spectroscopy studies confirmed the presence of a weak feature at 1660 cm^{-1} attributable to the poly(*N*-vinylpyrrolidone) stabilizer. The nitrogen microanalyses for these micrometre-sized latexes were typically 0.17–0.21%, which is consistent with a stabilizer content of *ca.* 1.5 mass% (this may be an upper limit value since it was assumed that the concentration of the nitrogen-containing Aliquat 336 surfactant was negligible). Using these data the adsorbed amount of PVP stabilizer on the latex particles was calculated to be approximately 4.5 mg m^{-2}. Recent X-ray photoelectron spectroscopy (XPS) studies have confirmed the presence of the poly(*N*-vinylpyrrolidone) stabilizer at the surface of our polystyrene latex particles.[27]

For the conducting polymer coating experiments the concentrations of pyrrole monomer and $FeCl_3$ oxidant were kept constant. The polypyrrole loading was controlled simply by varying the initial concentration, and hence the available surface area, of the polystyrene latex particles. The polypyrrole loadings on the latex composites determined from nitrogen microanalyses were in very good agreement with the theoretical values (Table 1). This result indicates that the pyrrole was quantitatively polymerized under the latex coating conditions. Beadle *et al.* also reported reasonable control over conducting polymer loading for the deposition of polyaniline onto low T_g chlorinated latexes.[16] However, the latex composites were obtained in the form of macroscopic precipitates in this latter study and larger differences between the theoretical and actual conducting polymer loadings were observed.

In the present study, there were no signs of gross precipitation except for sample 1 (Table 1), which contained a very high polypyrrole loading (*ca.* 51%). Subsequent inspection of

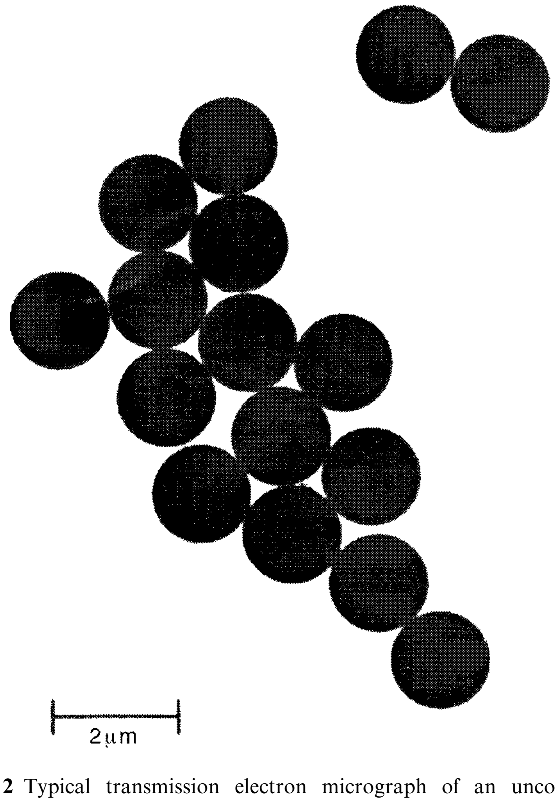

Fig. 2 Typical transmission electron micrograph of an uncoated, micrometre-sized poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex

Table 1 Effect of varying the total surface area of latex available for the deposition of polypyrrole (PPY) on the polypyrrole loading and layer thickness, the colloid stability and the electrical conductivity of the coated latex particles[a]

sample	latex surface area/m^2	theoretical PPY loading (mass%)	actual PPY loading (mass%)[b]	calculated PPY layer thickness/nm	colloid stability of PPY-coated latex[c]	σ^d/S cm^{-1}
1	0.4	52.7	51.1	164.3	unstable	3
2[e]	1.2	25.6	25.1	59.7	flocc'd	4
3	1.8	18.2	18.4	41.1	flocc'd	6
4[e]	2.3	15.4	16.6	36.5	flocc'd	3
5	3.6	10.0	9.9	20.5	stable	2
6	5.4	6.9	6.1	12.3	stable	2
7	7.1	5.3	5.6	11.2	stable	2
8	7.1	4.7	4.6	10.3	stable	0.8
9	10.0	3.4	3.5	7.8	stable	0.2
10	15.0	2.3	2.1	4.6	stable	6×10^{-2}
11	27.4	1.3	1.2	2.6	stable	3×10^{-3}
12	39.4	0.9	1.0	2.2	stable	$<10^{-6}$

[a]All polystyrene latexes were synthesized using PVP of $M_W=44\,000$ unless indicated otherwise. [b]Determined by reduced nitrogen content relative to polypyrrole 'bulk powder' using CHN elemental microanalyses. [c]Determined by DCP; flocc'd = flocculated. [d]Determined by the four-point probe method on compressed pellets at room temperature. [e]Stabilized using PVP of M_W 360 000. The 1.57 µm diameter polystyrene latex was used for samples 1, 3, 5, 6 and 7. The 1.64 µm diameter latex was used for samples 2 and 4 and the 1.80 µm diameter latex was used for samples 8–12.

this destabilized latex using SEM revealed both the original micrometre-sized polystyrene latex particles and also the distinctive, submicrometre-sized globular morphology of polypyrrole 'bulk powder' formed as a separate sub-phase [see Fig. 3(*a*)]. In contrast, as the latex surface area available for polypyrrole deposition was increased, little or no precipitation was observed and SEM studies showed no evidence for any separate polypyrrole subphase. At a polypyrrole loading of *ca.* 25% (sample 2 in Table 1) the polystyrene particles are uniformly coated with a globular polypyrrole overlayer [Fig. 3(*b*)]. For polypyrrole loadings lower than 10% (*e.g.*, sample 6) the morphology of the coated latexes was remarkably smooth and uniform [Fig. 3(*c*)], with no direct evidence for the deposited polypyrrole overlayer. It is interesting to compare this uniform polypyrrole morphology with the globular, inhomogeneous morphology reported by Armes *et al.* for micrometre-sized silica particles coated with polypyrrole or polyaniline overlayers at similarly low loadings.[10] It appears that the addition of a suitable polymeric steric stabilizer to maintain the dispersion stability of the colloidal substrate during conducting polymer deposition substantially affects the morphology of the overlayer.

The bulk densities of polystyrene and polypyrrole were determined to be 1.05 and 1.46 g cm^{-3} by helium pycnometry. Since SEM studies confirm that the polypyrrole overlayer is relatively smooth and uniform, for a given polystyrene latex diameter it is possible to calculate the average thickness, x, of the deposited polypyrrole overlayer using eqn. (1):

$$x=R\left[\left(\frac{M_2\rho_1}{M_1\rho_2}+1\right)^{1/3}-1\right] \tag{1}$$

where R is the radius of the uncoated latex particles, M_1 and ρ_1 are the mass fraction and density of the polystyrene component and M_2 and ρ_2 are the mass fraction and density of the polypyrrole component, respectively. For mass loadings of 1–10% the polypyrrole overlayer thicknesses lie in the range 2–20 nm (Table 1). According to Yamamoto and co-workers, PVP chains with a molecular mass of 360 000 (*i.e.* samples 2 and 4 in Table 1) have an adsorbed layer thickness of *ca.* 20–30 nm.[25] Obviously PVP chains of lower molecular mass would give rise to thinner layers of steric stabilizer. Thus it is apparent that, at lower mass loadings (<10%), the conducting polymer overlayer is either smaller than, or comparable to, the thickness of the adsorbed PVP layer. On the other hand, at loadings of 16.6% (sample 4 in Table 1) or higher, the polypyrrole overlayers become much less uniform and the assumptions made in deriving eqn. (1) are no longer valid.

It is interesting that polypyrrole should deposit so readily onto latex particles which are already well coated with a solvated, adsorbed layer of PVP stabilizer. In this regard, we note that the elegant XPS and time-of-flight secondary ion mass spectroscopy (TOF-SIMS) measurements on micrometre-sized polystyrene latexes reported by Deslandes *et al.* are consistent with a relatively 'patchy', rather than continuous, layer of PVP stabilizer.[28] Even when the surface concentration of PVP is relatively high the stabilizer chains are only anchored *via* a small number of monomer residues, with the rest of the chain being solvated as loops and tails, rather than adsorbed as trains at the particle surface. Thus, a substantial fraction of the total surface area of the sterically stabilized latex particles is actually available for the deposition of polypyrrole. Indeed, in our layer thickness calculations using eqn. (1) it is assumed that all of the latex surface becomes coated with conducting polymer.

The colloid stability of the polypyrrole-coated polystyrene latexes was assessed using DCP. Typical mass average particle size distributions of a coated and an uncoated latex are shown in Fig. 4. Since the polypyrrole overlayer is relatively thin (see above), the main peak in the size distribution of the coated latex approximately coincides with that of the uncoated precursor latex. However, there is both a secondary peak and also a distinct 'tail' to higher particle diameter in the size distribution curve of the coated latex. A simple calculation confirms that the position of the secondary peak corresponds to that expected for doublets (aggregation of two latex particles), with the tail corresponding to larger flocc structures (triplets, multiplets, *etc.*). Given the relatively high Hamaker constant reported for polypyrrole,[14] it is perhaps not surprising that the polypyrrole overlayer can interfere with the steric stabilization mechanism responsible for maintaining the colloid stability of the latex particles. However, provided that the polypyrrole overlayer is sufficiently thin (relative to the stabiliser layer thickness), it is nevertheless possible to minimize destabilization of the coated latex particles. For example, DCP size distribution data for a 1.6 µm polystyrene latex synthesized using a high molecular mass (360 000) PVP stabilizer coated with *ca.* 10% polypyrrole by mass is depicted in Fig. 5(*a*). This size distribution contains very little evidence for flocculation and is very similar to that of the original uncoated latex. On the other hand, a 1.6 µm latex with a similar polypyrrole loading synthesized using a low molecular mass (M_W 44 000) PVP stabilizer (10% polypyrrole by mass) is clearly appreciably flocculated [Fig. 5(*b*)]. It is well known that increasing the molecular mass of a homopolymer stabilizer provides a thicker steric barrier towards particle aggregation. Clearly, the additional layer thickness provided by a higher molecular mass PVP stabilizer

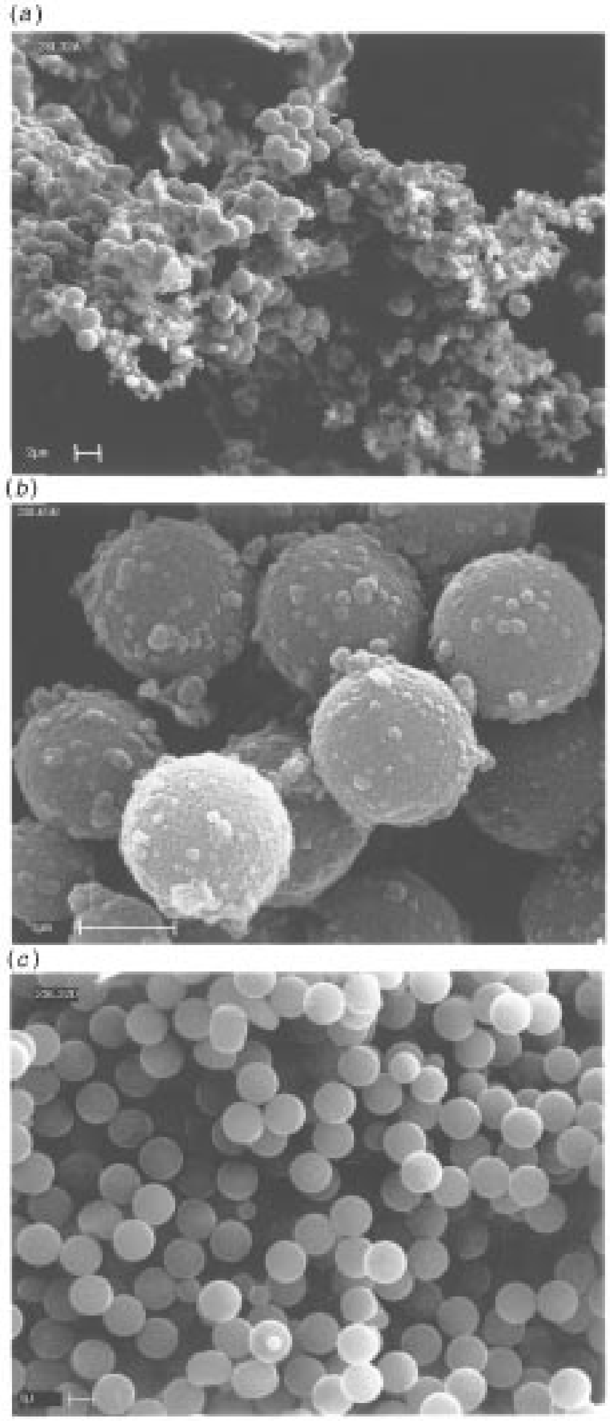

Fig. 3 Scanning electron micrographs of a polypyrrole-coated polystyrene latex with (*a*) a relatively high polypyrrole loading (51.1%); (*b*) an intermediate polypyrrole loading (25.1%); (*c*) a relatively low polypyrrole loading (6.1%). Note the absence of any globular polypyrrole morphology at the lowest loading

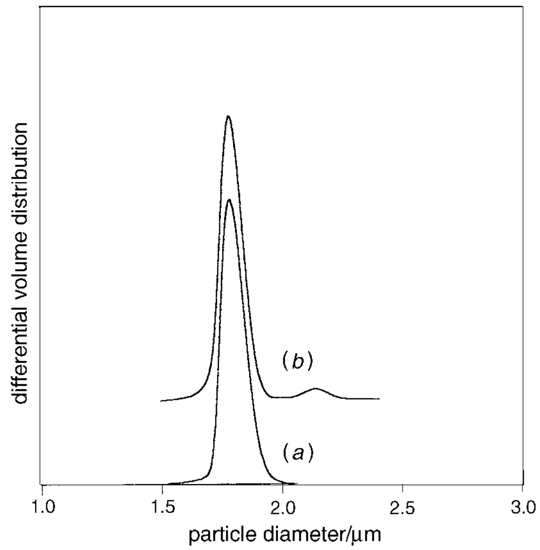

Fig. 4 Mass-average particle size distribution curves obtained for (*a*) an uncoated polystyrene latex and (*b*) a polypyrrole-coated latex (polypyrrole loading of 4.6%; sample 11 in Table 1) obtained using the disk centrifuge

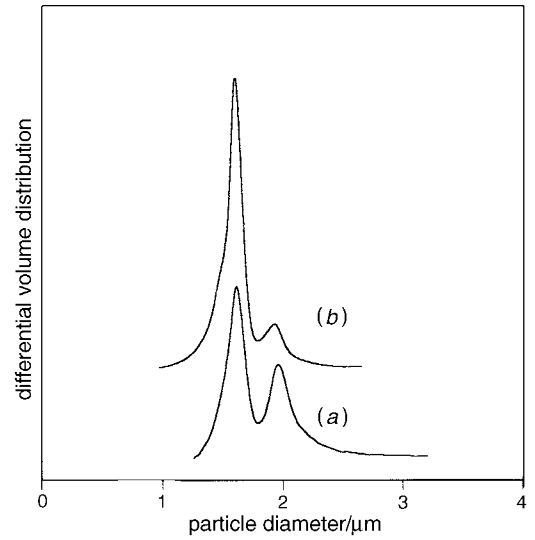

Fig. 5 Mass-average particle size distribution curves obtained for two polypyrrole-coated polystyrene latexes obtained using the disk centrifuge: (*a*) PVP stabilizer molecular mass = 360 000 and (*b*) PVP stabilizer molecular mass = 44 000. The polypyrrole loading in each case is approximately 10% by mass.

can lead to a considerable improvement in the degree of dispersion of the coated latex particles. A more quantitative assessment of the influence of the polypyrrole overlayer on the latex colloid stability would require accurate measurement of the thickness of the adsorbed PVP stabilizer layer. Unfortunately, given the relatively large particle size of the polystyrene latexes, this is an experimentally inaccessible parameter since the PVP layer thickness is considerably less than the observed standard deviation of the latex size distribution. Finally, it was noted that ultrasonication of the coated latexes just prior to DCP analysis temporarily improved their degree of dispersion, *i.e.* the proportion of aggregates decreased relative to the singlet peak.

The relationship between log conductivity and conducting polymer volume fraction for the polypyrrole-coated polystyrene particles is shown in Fig. 6(*a*). A remarkably low percolation threshold of *ca.* 1–2 vol. % is observed for these latex composites, presumably since the conductive component is located exclusively on the outside of the latex particles. SEM studies on fractured pellets have confirmed that, although somewhat deformed by the pelletisation process, the latex particles remain intact. Thus, the coated particles effectively behave like micrometre-sized polypyrrole particles and efficient charge transport through the material can occur without significant interference from the underlying electrically insulating polystyrene component (Fig. 7). This conductivity data stands close comparison with the best (lowest) percolation thresholds claimed for other conducting polymers such as polyaniline.[29,30] Similar results have been reported by

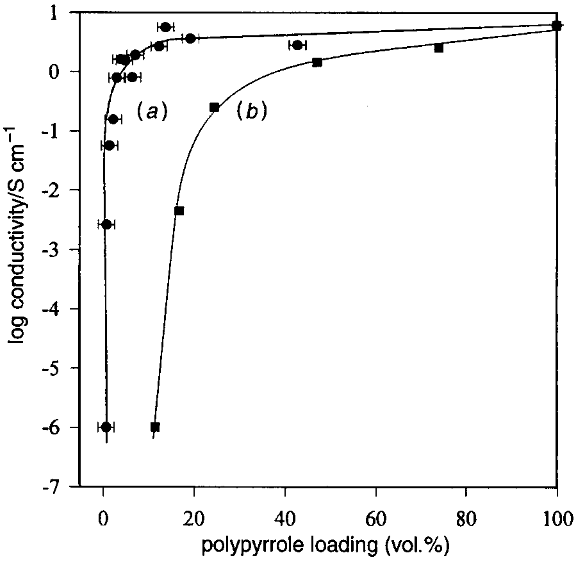

Fig. 6 Variation of conductivity with polypyrrole loading for (*a*) polypyrrole-coated polystyrene latex composites and (*b*) heterogeneous mixtures of the dried polystyrene latex mixed with polypyrrole bulk powder. Note the much lower percolation threshold observed in the former system.

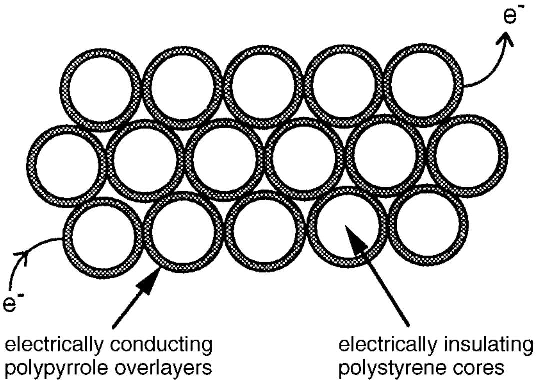

Fig. 7 Schematic representation of charge transport between polypyrrole-coated polystyrene latex particles at the microscopic level. Interparticle charge carrier transport can occur *via* surface conduction in the polypyrrole overlayer with minimal interference from the underlying electrically insulating polystyrene cores.

Yoshino's group for non-colloidal 35 μm polyethylene spheres, although somewhat lower 'plateau' conductivities were obtained by these workers.[17] As a control experiment, heterogeneous mixtures of pre-weighed quantities of dried uncoated polystyrene latex combined with polypyrrole 'bulk powder' (synthesized as a precipitate in the absence of latex) were prepared. These control samples gave 'classical' percolation behaviour [Fig. 6(*b*)], with a conductivity threshold of *ca.* 20 vol. %.[31] Thus, there is no doubt that the 'core–shell' morphology of the polypyrrole-coated polystyrene latexes is responsible for the unusual conductivity behaviour of these materials.

IR spectra of a dried polystyrene latex and a polypyrrole-coated polystyrene latex are shown in Fig. 8. The spectrum for the uncoated latex is typical for that of polystyrene, with an additional weak feature at *ca.* 1660 cm^{-1} attributable to the pyrrolidone carbonyl of the PVP stabilizer. The coated latex (polypyrrole loading *ca.* 5.6% by mass) contains several additional strong bands at 1549, 1316, 1186 and 910 cm^{-1} due to the doped polypyrrole component.[1,3] Even allowing for polypyrrole being a strong IR absorber, these bands seem rather intense given the relatively low concentration of the conducting polymer component. As a control experiment, an IR spectrum of a heterogeneous mixture comprising 94% uncoated polystyrene latex and 6% polypyrrole 'bulk powder' was recorded. The polypyrrole bands are barely detectable in this latter spectrum, even though the polypyrrole content is actually slightly higher than that of the coated latex. This suggests that the 'core–shell' morphology of the polypyrrole-coated polystyrene latex particles leads to enhanced IR absorption by the conducting polymer component. This observation is probably related to the latex particle size being similar to the wavelength of the IR radiation. We have observed similar 'enhanced absorption' effects in the Raman spectra of these composite particles; these results are presented in the following paper.[32]

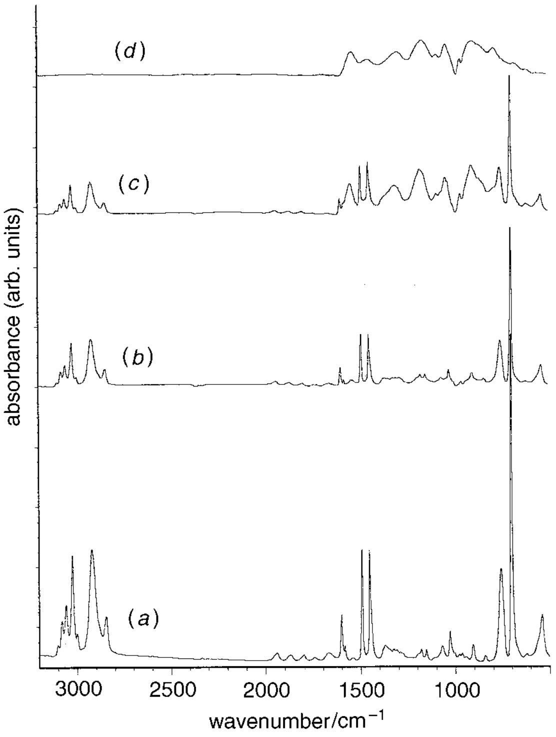

Fig. 8 FTIR spectra of (*a*) uncoated polystyrene latex particles; (*b*) heterogeneous mixture of 6.0% polypyrrole mixed with 94.0% polystyrene latex particles; (*c*) polypyrrole-coated polystyrene latex particles (polypyrrole loading 5.6%); (*d*) polypyrrole chloride bulk powder. The absorption bands due to polypyrrole are strong in spectrum (*c*) but much weaker in spectrum (*b*). This is consistent with a core–shell particle morphology for the latex composites.

It is well known that the environmental stability of polypyrrole doped with chloride anions is relatively poor: significant conductivity decay over a period of a few days is not uncommon.[33] On the other hand, much better conductivity stability is usually found for polypyrrole doped with aromatic sulfonate anions. In particular, Kuhn *et al.* at the Milliken Research Corporation have developed polypyrrole syntheses involving aromatic sulfonate dopant anions which have been optimized for coating high surface area textile fibres.[34] This Milliken coating protocol was utilized in the present study in order to coat the polystyrene latex particles. Similar polypyrrole loadings and conductivities were obtained, but the coated latexes exhibited somewhat poorer colloid stabilities as measured by the DCP technique. However, the long-term conductivity stability of the aromatic sulfonate-doped polypyrrole overlayer is somewhat improved compared to that of the chloride-doped polypyrrole material (Fig. 9). The effect of using chemical oxidants other than $FeCl_3$ was also examined. Both $(NH_4)_2S_2O_8$ and H_2O_2–HBr–Fe^{3+} were used to synthesize polypyrrole-coated polystyrene latexes (Table 2). Similar conducting polymer loadings were obtained, but conductivities

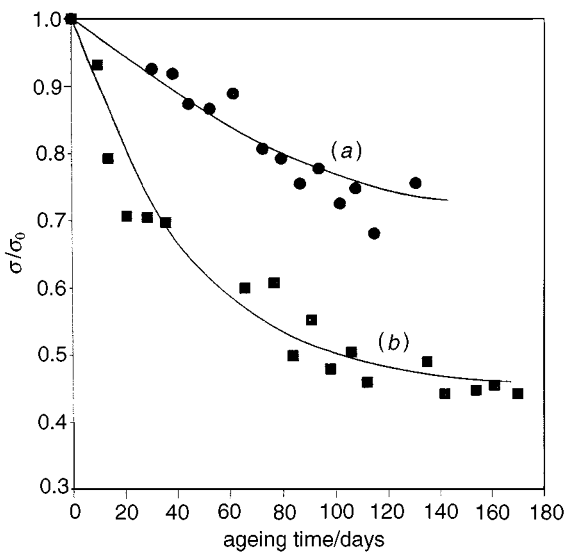

Fig. 9 Typical conductivity decay curves for pressed pellets of polypyrrole-coated polystyrene latex particles: (*a*) aromatic sulfonate dopant anions according to ref. 32 and (*b*) chloride dopant anions. The polypyrrole loadings are 5.4% and 4.4% by mass respectively.

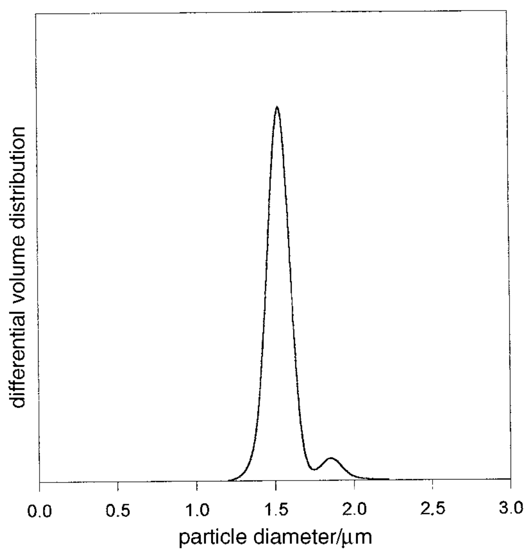

Fig. 10 Mass-average particle size distribution curve obtained using the disk centrifuge for a polypyrrole-coated, polyelectrolyte-stabilized polystyrene latex (the polypyrrole loading is 5.0% by mass). The polyelectrolyte stabilizer is a cationic PDMAEMA–PMMA block copolymer (see main text).

were somewhat lower, probably due to over-oxidation of the polypyrrole chains.[35]

Finally, the deposition of conducting polymers other than polypyrrole has also been investigated. Both polyaniline- and poly(3,4-ethylenedioxythiophene)-coated latexes have been synthesized with conducting polymer loadings of 5–10 mass%. DCP analysis confirmed that these coated latexes also have reasonable degrees of dispersion. Pressed pellet conductivities were as high as $1\ \mathrm{S\ cm^{-1}}$ for the polyaniline-coated latexes and $10^{-2}\ \mathrm{S\ cm^{-1}}$ for the poly(3,4-ethylenedioxythiophene)-coated latexes.

All of the examples of conducting polymer-coated latexes claimed in the DSM patent[12] involve the use of a non-ionic polymeric stabilizer [either poly(ethylene oxide) or cellulosic derivatives] which is chemically grafted onto the surface of the latex particles. Two obvious questions which arise are the following: (1) Can polyelectrolytes act as effective steric stabilizers for the deposition of polypyrrole? (2) Is a chemically grafted stabilizer essential for the successful deposition of polypyrrole without significant loss of colloid stability? With regard to the first question, the successful coating of a PDMAEMA–PMMA-stabilized polystyrene latex with *ca.* 5% polypyrrole by mass (Fig. 10) confirms that this cationic polyelectrolyte block copolymer acts as a reasonably effective steric stabilizer. Thus, a non-ionic steric stabilizer does not appear to be an essential pre-requisite. In most of the present work we have utilized poly(*N*-vinyl pyrrolidone): according to Deslandes *et al.* this steric stabilizer probably becomes grafted onto the latex particles during the free-radical dispersion polymerization of styrene.[28] Thus, in order to address the second question we attempted to coat an aqueous dispersion of 'naked', charge-stabilized, 1 μm polystyrene latex (Fig. 11). In the absence of any steric stabilizer layer, significant aggregation of this latex occurred soon after addition of the pyrrole monomer [Fig. 12(*a*)]. However, physical adsorption of an excess of PVP ($M_W = 44\,000$) onto this charge-stabilized latex, followed by addition of the $FeCl_3$ and pyrrole reagents, allowed the preparation of a polypyrrole-coated polystyrene latex with reasonable colloid stability [Fig. 12(*b*)] and a conducting polymer loading of *ca.* 8.8 mass%. This result confirms that a chemically grafted stabilizer layer is not essential: a merely physically adsorbed stabilizer is sufficient to allow good control over the polypyrrole deposition process. Moreover, it suggests a more general coating protocol, which in principle could be extended to include colloidal substrates other than polymer latexes, *e.g.* inorganic oxides, silicates, sulfides, *etc.*

Conclusions

In summary, it has been shown that sterically stabilized, micrometre-sized polystyrene latexes can be readily coated with a very thin conducting polymer overlayer. In the case of polypyrrole, good control over the conducting polymer loading has been demonstrated simply by varying the initial concentration of latex particles used in the coating protocol. At low loadings (<10 mass%) the deposited polypyrrole layer is very smooth and uniform. The intensity enhancement of IR bands attributable to polypyrrole and the observation of an anomalously low conductivity percolation threshold are both consistent with a 'core–shell' morphology for the composite particles. The disk centrifuge has been shown to be an excellent technique for assessing the colloid stability of the coated particles, which are usually weakly flocculated. However, if the polypyrrole

Table 2 Polypyrrole (PPY) mass loadings, colloid stability and pellet conductivities for polypyrrole-coated polystyrene latexes synthesized using alternative oxidant systems

sample	oxidant system	PVP molecular mass/g mol^{-1}	PPY loading (mass%)[a]	colloid stability of PPY-coated latex[b]	$\sigma^c/\mathrm{S\ cm^{-1}}$
13	H_2O_2–HBr–Fe^{3+}	44 000	7.3	stable	0.1
14	$(NH_4)_2S_2O_8$	44 000	8.9	stable	0.2
15	'Milliken'	360 000	8.1	flocc'd	2.0

[a]Determined by reduced nitrogen content relative to polypyrrole 'bulk powder' using CHN elemental microanalyses. [b]Determined by DCP. [c]Determined by the four-point probe method on compressed pellets at room temperature. Samples 13 and 14 were prepared with the 1.57 μm diameter polystyrene latex and sample 15 with the 1.64 μm diameter latex.

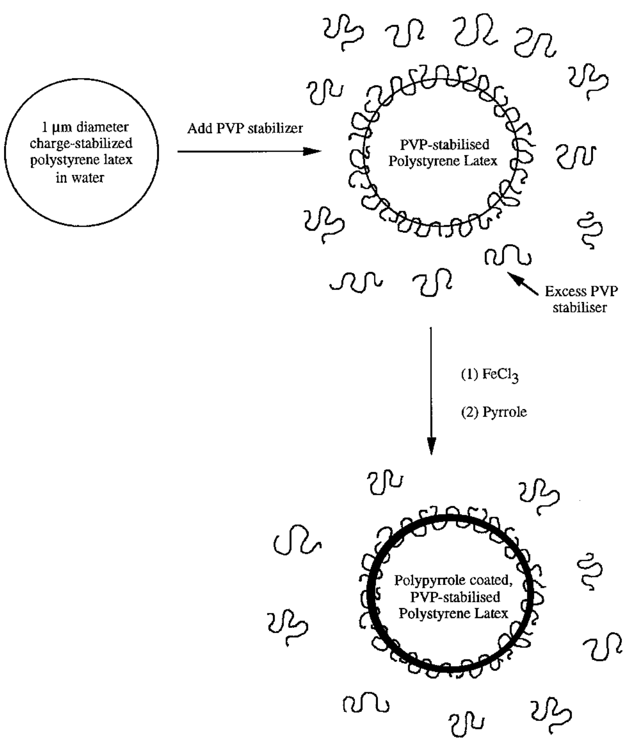

Fig. 11 Schematic representation of the synthesis of polypyrrole-coated polystyrene latexes using a physically adsorbed poly(*N*-vinylpyrrolidone) stabilizer

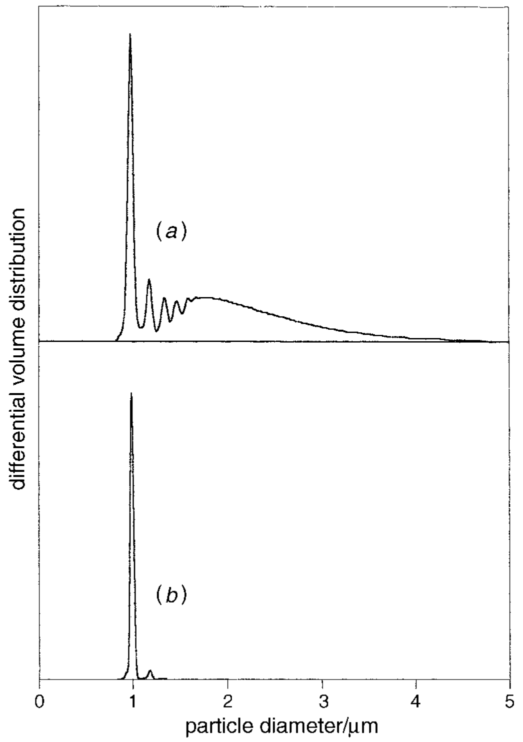

Fig. 12 Mass-average particle size distribution curves obtained using the disk centrifuge for (*a*) a polypyrrole-coated, charge-stabilized polystyrene latex of 1 µm diameter coated in the absence of any PVP stabilizer and (*b*) the same latex coated with a thin overlayer of polypyrrole using physically adsorbed PVP to provide a steric stabilizer layer. The polypyrrole loading on both these coated latexes is approximately 11% by mass. Note that a much higher degree of dispersion is obtained in the presence of the PVP stabilizer.

overlayer is relatively thin compared to the steric stabilizer layer then a reasonable degree of dispersion can be achieved. Higher polypyrrole mass loadings generally result in higher electrical conductivity but poorer colloid stability. Nevertheless, it is possible to obtain conductivities in the 10^{-1}–10^{0} S cm^{-1} range and colloid stabilities at polypyrrole loadings of 3–6%. Incorporation of aromatic sulfonate anions into the pyrrole polymerization leads to improved conductivity stability but more flocculated dispersions. Other conducting polymers such as polyaniline and poly(3,4-ethylenedioxythiophene) can also be deposited onto polystyrene latexes without significant loss of colloid stability. With regard to the nature of the steric stabilizer layer, cationic polyelectrolytes such as PDMAEMA–PMMA can also act as effective steric stabilizers. Thus, a non-ionic steric stabilizer is not a prerequisite for the successful synthesis of conducting polymer-coated latexes. Finally, it has been shown that a chemically grafted steric stabilizer is not essential: under appropriate conditions a physically adsorbed poly(*N*-vinylpyrrolidone) stabilizer can prevent significant particle aggregation and hence allow good control over the conducting polymer deposition process.

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