Surface characterization of micrometre-sized, polypyrrole-coated polystyrene latexes: verification of a 'core–shell' morphology†

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Micrometre-sized, polypyrrole-coated polystyrene latexes with various conducting polymer loadings have been extensively characterized using X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (TOF-SIMS), Raman and UV–VIS reflectance spectroscopy, scanning force microscopy (SFM) and scanning electron microscopy (SEM). Both XPS and TOF-SIMS studies are consistent with relatively uniform, chloride-doped polypyrrole overlayers. Raman studies also indicated a 'core–shell' morphology since only bands attributable to polypyrrole were observed; no evidence was found for the underlying polystyrene component even at the lowest polypyrrole loadings. This is most likely due to remarkably efficient attenuation of the polystyrene bands by the highly absorbing polypyrrole overlayer. UV–VIS reflectance spectroscopy studies confirmed that a coated latex had a much lower reflectance (higher absorbance) than a heterogeneous admixture of polypyrrole and polystyrene with a similar polypyrrole content. High-resolution images of the polypyrrole overlayer nanomorphology were obtained using SFM. At low polypyrrole loadings (1.0 mass%) the overlayer was relatively smooth and uniform, but higher loadings (8.9 mass%) resulted in a rougher, more globular morphology. Finally, the underlying polystyrene latex 'core' was quantitatively removed by solvent extraction. SEM studies of the polypyrrole residues revealed a 'broken egg-shell' morphology, thus providing irrefutable evidence for the 'core–shell' morphology of the original polystyrene/polypyrrole particles.

Recently we reported[1,2] coating micrometre-sized, sterically stabilized polystyrene latex particles with ultrathin overlayers of polypyrrole (Fig. 1). Polystyrene was selected as a 'model' colloidal substrate since it has a relatively high T_g (*i.e.* the particles are rigid and non-deformable) and latexes can be readily synthesized with narrow size distributions over a wide particle size range (50 nm–10 µm).[3,4] Variation of the polystyrene particle concentration (and hence total surface area of latex) at fixed pyrrole polymerization conditions proved to be a very effective method for controlling the conducting polymer loading on the latex particles. Scanning electron microscopy (SEM) studies confirmed that, at polypyrrole mass loadings of $<10\%$, the conducting polymer overlayer had a relatively smooth and featureless morphology. FTIR spectroscopy studies on the dried composite particles suggested that the absorption bands due to the polypyrrole overlayer component were significantly enhanced compared to those of heterogeneous mixtures of polypyrrole 'bulk powder' and polystyrene latex. Similarly, conductivity measurements on pressed pellets of the dried, coated latexes indicated an anomalously low conductivity percolation threshold. Both spectroscopic and conductivity data were consistent with a 'core–shell' latex morphology. Potential applications for these micrometre-sized polypyrrole-coated polystyrene composite latexes include new stationary phases for electrochromatography[5] or possibly novel 'marker' particles for visual agglutination diagnostic assays.[6] In addition, polypyrrole-coated polystyrene latexes of submicrometre dimensions have recently proved[7] to be a useful model system for understanding the behaviour of polypyrrole-coated film-forming latexes such as those currently being developed[8] by DSM Research for antistatic and anticorrosion applications.

Recently, in collaboration with Chehimi and co-workers, one of our micrometre-sized polypyrrole-coated polystyrene latexes was extensively examined by X-ray photoelectron spectroscopy (XPS).[9] This study confirmed that the surface of this thickly coated latex (comprising 8.7 mass% polypyrrole) was predominantly polypyrrole-rich, with surprisingly little evidence for either the underlying polystyrene component or the poly(*N*-vinylpyrrolidone) stabilizer. It was concluded that the polypyrrole overlayer on the polystyrene latex particles was relatively uniform, rather than 'patchy'.

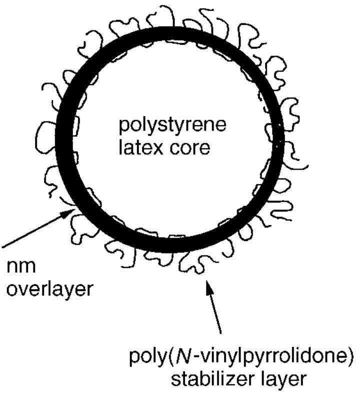

Fig. 1 Schematic representation of an isolated, micrometre-sized, polypyrrole-coated polystyrene latex particle

In the present work we describe a detailed study of the surface composition and nanomorphology of these micrometre-sized, polypyrrole-coated polystyrene latexes using six experimental techniques, namely XPS, time-of-flight secondary ion mass spectroscopy (TOF-SIMS), Raman spectroscopy, UV–VIS reflectance spectroscopy, scanning force microscopy (SFM) and SEM.

Experimental

Polystyrene latex synthesis and polypyrrole coating protocol

The general latex synthesis procedure is outlined in the preceding paper.[2] The two latexes were sized by disk centrifuge

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photosedimentometry (DCP) using a Brookhaven BI-DCP instrument, operating in the line start mode as described previously.[2] DCP studies confirmed that the two latexes had narrow size distributions and were of very similar size: the mass-average particle diameters were 1.57 ± 0.12 and 1.80 ± 0.06 µm, respectively. Throughout this paper these latexes are referred to as the '1.6 µm' and the '1.8 µm' latexes. These DCP sizes were confirmed by transmission electron microscopy (TEM) (Hitachi 7100 instrument), and SEM (Leica Stereoscan 420 instrument) on gold-coated dried latexes. A portion of each sample was oven-dried at 60 °C overnight prior to CHN elemental microanalyses at an independent laboratory (Medac Ltd at Brunel University, UK). The general polypyrrole coating protocol is also outlined in the preceding paper.[2]

Solvent extraction experiments

Excess THF (20 ml) was added to *ca.* 100 mg of a dried polypyrrole-coated polystyrene latex (1.6 µm polystyrene latex; 6.5% polypyrrole loading by mass) at room temperature and this solution was left to stand overnight. The resulting black residues were filtered, washed with THF and dried in an oven overnight at 60 °C. The residues yield was consistent with the mass loss expected for the polystyrene component. The chemical composition and morphology of the residues were analyzed by FTIR spectroscopy and SEM respectively (see later).

Characterization of polypyrrole-coated polystyrene latexes

Chemical composition and conductivity measurements. The polypyrrole loadings of each of the coated latexes were determined by comparing their nitrogen contents to that of the corresponding uncoated polystyrene latex (the nitrogen contents were 0.17 and 0.18% for the 1.6 and 1.8 µm latexes, respectively), and conventional polypyrrole 'bulk powder' (average nitrogen content of $16.5 \pm 0.5\%$) synthesized in the absence of latex particles. The conductivities (σ) of compressed pellets of the polypyrrole-coated polystyrene latexes were determined using standard four-point probe techniques at room temperature. It is estimated that the random error associated with such measurements is *ca.* 10%, with a systematic error of *ca.* 5–10%.

Time-of-flight secondary ion mass spectrometry. Spectra were acquired using a VG Scientific Type 23 system. This instrument was equipped with a single stage reflectron time-of-flight analyser and a MIG300PB pulsed liquid-metal (^{69}Ga) ion source. Static SIMS conditions[10] were employed for the analyses (*i.e.* $<10^{13}$ ions cm^{-2} per analysis) which was accomplished using a primary ion beam pulsed at 20 kHz and 25 ns. The beam was rastered over an area of *ca.* 1 mm^2 at a rate of 50 frames s^{-1}, and both positive and negative spectra were acquired over a mass range of 5–800 u. Specimens were prepared by decanting a small amount of the colloidal dispersion onto 1 cm diameter sample stubs and allowing the aqueous phase to evaporate; this provided a uniform coverage of the latex particles on the stub and no signals from the underlying stub were evident in either the SIMS or XPS spectra.

X-Ray photoelectron spectroscopy. XPS spectra were collected using a VG Scientific ESCALAB Mk II spectrometer. This was operated in the constant analyzer mode (CAE) using pass energies of 50 eV for survey spectra and 20 eV for the high-resolution spectra. Al-Kα radiation was employed at an anode power of 420 W. For spectral acquisition and subsequent data processing the spectrometer was controlled by a VGS 5000 data system based on a DEC PDP 11/73 computer. Quantification was achieved using peak areas and Wagner sensitivity factors and the manufacturer's software. Specimen preparation was achieved in a similar manner to that used for the TOF-SIMS experiments.

Raman spectroscopy. Raman spectra were recorded using a Bruker FRA 106 spectrometer. Excitation was provided by an Adlas Nd:YAG laser at a wavelength of 1064 nm, operating at 30 mW for the polypyrrole-containing samples and 300 mW for the uncoated polystyrene latex. Data were acquired at a resolution of 4 cm^{-1} and spectra were averaged over 2000 scans.

UV–VIS reflectance spectroscopy. A diffuse reflectance accessory (PE 60 mm integrating sphere) was used in conjunction with a Lambda 9 Perkin-Elmer UV–VIS spectrophotometer. The dried powders were mounted onto double-sided adhesive tape. Control experiments on uncoated, micrometre-sized polystyrene latex indicated *ca.* 100% reflectance for this system in the range 350–800 nm, and also confirmed that there was no significant contribution to the UV–VIS spectrum from the underlying adhesive tape. Single-scan spectra were recorded at a scan speed of 60 nm min^{-1}. Reflectance measurements were performed against a barium sulfate standard, which had been previously referenced to an NPL-calibrated opal standard.

Scanning force microscopy. Samples for SFM studies were prepared by drying a small drop of the aqueous latex dispersion onto a very flat Si(100) substrate. This procedure produced mechanically stable deposits which were analyzed by SFM in the contact mode. Standard microfabricated Si_3N_4 cantilevers (100 µm in length with a spring constant of 0.40 N m^{-1}) with integrated pyramidal Si_3N_4 4 µm tips were employed as force sensors for SFM imaging. The apparatus used in this research was a Nanoscope II SFM (Digital Instruments Inc, Santa Barbara, CA, USA), which has been described in detail elsewhere.[11] The samples were scanned at constant force in the range 10^{-7}–10^{-8} N. SFM images from uncoated latex particles demonstrated good reproducibility due to a relatively strong attractive interaction between the deposited particles. On the other hand, SFM imaging of the polypyrrole-coated latex particles was much more difficult, probably because of repulsive interaction between the particles as a result of electric charge accumulation during scanning. Such charging could arise from direct mechanical interaction between the insulating Si_3N_4 tip and the electrically conductive particles mounted on the Si wafer, covered by a thin insulating surface layer of oxidized silicon. It should be noted that the image analysis software is designed for planar substrates and is not well suited to features with high curvature such as latex particles. In the present study relative morphological differences between samples are emphasized and no attempt has been made to quantify surface roughness.

FTIR spectroscopy. FTIR spectra (KBr disk) were recorded using a Nicolet Magna 550 Series II research-grade instrument. Spectra were typically averaged over 64 scans at 4 cm^{-1} resolution.

Scanning electron microscopy. Morphology studies were carried out using a Leica Stereoscan 420 instrument operating at 30 kV. The samples were mounted on a double-sided adhesive carbon disc and sputter-coated with a thin layer of gold to prevent sample charging problems.

Results and Discussion

The latex syntheses *via* dispersion polymerization using a poly(N-vinylpyrrolidone) stabilizer in alcoholic media proved to be reasonably repeatable. Two polystyrene latexes of *ca.* 1.6 and 1.8 µm diameter were obtained in high yield. For the conducting polymer coating experiments the synthesis conditions (*i.e.* the concentrations of the pyrrole and $FeCl_3$ reagents) were held constant and the latex particle concentration was systematically varied in order to control the final polypyrrole loading.[1,2] The particle size, conducting polymer loadings and electrical conductivities of the four polypyrrole-coated polystyrene latexes examined in this study are summarized in Table 1. The polypyrrole overlayer thicknesses were calculated as described previously.[2] The overlayer was assumed to be uniform and the polypyrrole and polystyrene densities were taken to be 1.46 and 1.05 $g\ cm^{-3}$, respectively. Most of the characterization work described in the present study was carried out on samples 1 and 4, which are coated with relatively thick and relatively thin polypyrrole overlayers, respectively. The polypyrrole loading in sample 1 is above the 'knee' in the conductivity percolation threshold curve for these composite particles,[2] and therefore the conductivity of this material is comparable to that of polypyrrole bulk powder (1 $S\ cm^{-1}$). In contrast, the polypyrrole loading in sample 4 is below the percolation threshold and this sample has a much lower conductivity ($<10^{-6}\ S\ cm^{-1}$).

X-Ray photoelectron spectroscopy

The survey spectrum of an uncoated 1.8 µm diameter poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex is shown in Fig. 2. An N 1s peak is clearly visible and is most likely due to the poly(*N*-vinylpyrrolidone) stabilizer at the surface of the latex particles. However, it is impossible to exclude the possibility of contributions to the N 1s signal from AIBN-initiated polystyrene chains and/or the nitrogen-containing cationic surfactant (Aliquat 336) used in the polystyrene latex syntheses. If we assume that these species do not significantly affect the microanalytical nitrogen content of the latex, a stabilizer content of *ca.* 1.5% can be calculated. This is consistent with the observation of a very weak feature due to the pyrrolidone carbonyl group at *ca.* 1660 cm^{-1} in the IR spectrum of this material.[2] Applying appropriate sensitivity factors we estimate an N/C ratio of 0.031 from the XPS spectrum of the uncoated latex. This value is lower than that determined by XPS for the poly(*N*-vinylpyrrolidone) stabilizer alone, which suggests that the surface coverage of the latex particles by the stabilizer is incomplete. This conclusion is in agreement with studies reported by both Deslandes *et al.*[12] and Chehimi and coworkers.[9]

According to their respective structural formulae the theoretical N/C ratio in polypyrrole is *ca.* 0.25, whereas the N/C ratio of poly(*N*-vinylpyrrolidone) is somewhat lower at 0.166. In XPS studies of conducting polymers the surface carbon signal is generally somewhat more intense than expected on the basis of elemental microanalyses. This is most likely due to the relatively high surface energies of these materials.[14] Thus, precise agreement between N/C ratios calculated from XPS data and structural formulae is not necessarily expected. Nevertheless, if the polypyrrole were present as an overlayer on the latex surface, the XPS N/C ratios of the two coated latexes would be expected to be higher than that of the uncoated latex. This is indeed the case. The other survey spectra depicted in Fig. 2 are for two polypyrrole-coated polystyrene latexes with polypyrrole mass loadings of 1.0 and 8.9% and N/C ratios of 0.052, and 0.085, respectively (samples 4 and 1 in Table 1). It is noteworthy that the reduced N/C ratio found for the lower mass loading is consistent with the polypyrrole overlayer thickness being less than the XPS sampling depth of 2–5 nm for this sample.

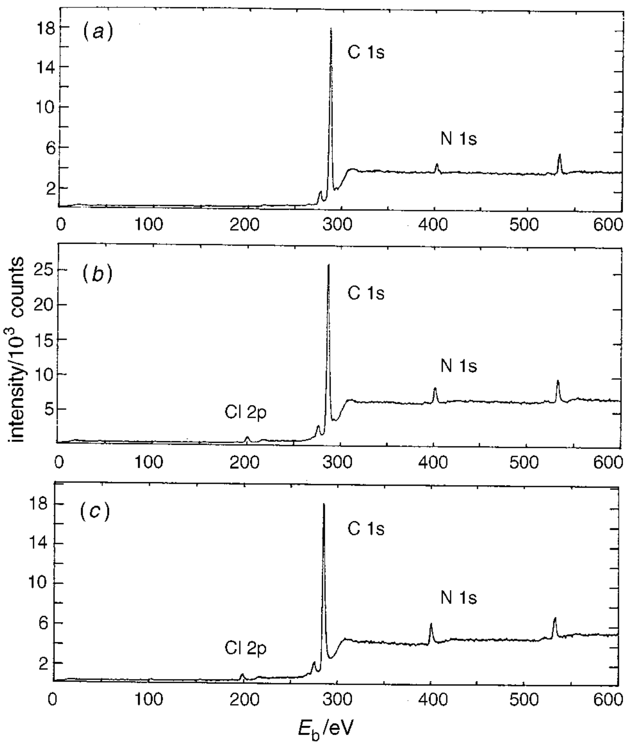

Fig. 2 X-Ray photoelectron survey spectra of: (*a*) an uncoated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex of 1.8 µm diameter; (*b*) and (*c*) polypyrrole-coated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latexes of 1.8 µm diameter with polypyrrole mass loadings of 1.0 and 8.9% respectively (see samples 4 and 1 in Table 1)

Close inspection of the XPS spectra of the coated latexes reveals additional signals due to Cl 2p. This indicates that the cationic polypyrrole chains are doped with chloride anions (originating from the $FeCl_3$ oxidant used to polymerize the pyrrole). From the XPS spectra the Cl/N atomic ratios were estimated to be 0.21 and 0.27 at polypyrrole mass loadings of 1.0 and 8.9%, respectively. Taking into account the likelihood of surface degradation and concomitant loss of dopant species, these values are in reasonable agreement with the normally accepted doping range for polypyrrole (0.25–0.33). There is no evidence for any Fe signals in the spectral region from 708 to 720 eV, which suggests that these two latexes are significantly

Table 1 Summary of the particle size, conducting polymer loading and electrical conductivity of the polypyrrole-coated polystyrene (PS) latexes examined in this study

sample	PS latex diameter[a]/µm	nitrogen content of latex[b] (mass%)	polypyrrole loading[b] (mass%)	polypyrrole layer thickness[c]/nm	σ^d/S cm^{-1}
1	1.8	1.71	8.9	21	1
2	1.6	1.25	6.5	13	3
3	1.8	0.94	4.6	10	0.8
4	1.8	0.34	1.0	2	$<10^{-6}$

[a] As measured by DCP (confirmed by electron microscopy). [b] From CHN elemental microanalyses. Polypyrrole loadings were obtained by calculating reduced nitrogen contents relative to that of polypyrrole 'bulk powder' (16.5% N) prepared in the absence of latex. [c] Calculated assuming a uniform polypyrrole overlayer as described in ref. 2. [d] Four-point probe measurements on compressed pellets at room temperature.

less contaminated with iron salt(s) than the polypyrrole-coated polystyrene latex examined by Chehimi and co-workers.[9]

High-resolution C 1s XPS spectra of the same three latexes are shown in Fig. 3. A 'shake-up' satellite at *ca.* 291.5–292.0 eV is clearly visible in the spectra of both the uncoated latex and also the coated latex which contains 1.0% polypyrrole (sample 4). This feature has been previously assigned to a π–π^* transition for the aromatic rings of the polystyrene component.[9] Its presence suggests that the overlayer is either very thin (*i.e.* less than the XPS sampling depth) and/or is rather 'patchy'. This observation is also consistent with the reduced N/C ratio for this sample (see above). No 'shake-up' satellite is visible in the C 1s spectrum of the latex containing 8.9% polypyrrole (sample 1), which suggests that the overlayer in this latter sample is sufficiently thick and/or more uniform to obscure the underlying polystyrene latex. Similar observations were reported by Chehimi and co-workers, who examined a polystyrene latex coated with a similarly thick overlayer of polypyrrole.[9]

Time-of-flight secondary ion mass spectrometry

Fig. 4 depicts three 'negative ion' TOF-SIMS spectra in the low mass range. The first spectrum is of the uncoated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex of 1.8 µm diameter. This spectrum is identical to that obtained for the pristine poly(*N*-vinylpyrrolidone) stabilizer, which is consistent with this component being located at the latex surface. There is a mass peak at 26 u which is assigned to CN^- fragments from the pyrrolidone unit of the stabilizer. The second spectrum is that of a polypyrrole chloride 'bulk powder' synthesized by conventional precipitation polymerization in the absence of any latex. A peak at 26 u is again prominent: this has been previously assigned to the CN^- anion and is therefore characteristic of polypyrrole.[14] It is noteworthy that, in this spectrum, the 26/25 peak ratio is greater than unity (the 25 u peak is assigned to the C_2H^- anion). In addition, there are two peaks at 35 and 37 which are attributable to ^{35}Cl and ^{37}Cl. The third spectrum is of a polypyrrole-coated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex of 1.8 µm diameter (8.9% polypyrrole loading by mass; sample 1). Again, the 26/25 peak ratio is greater than unity and there are two strong peaks due to the isotopic chloride anions. Thus these TOF-SIMS spectra are consistent with the XPS data and further support the hypothesis that chloride-doped polypyrrole is formed as an overlayer on the surface of the polystyrene latex particles.

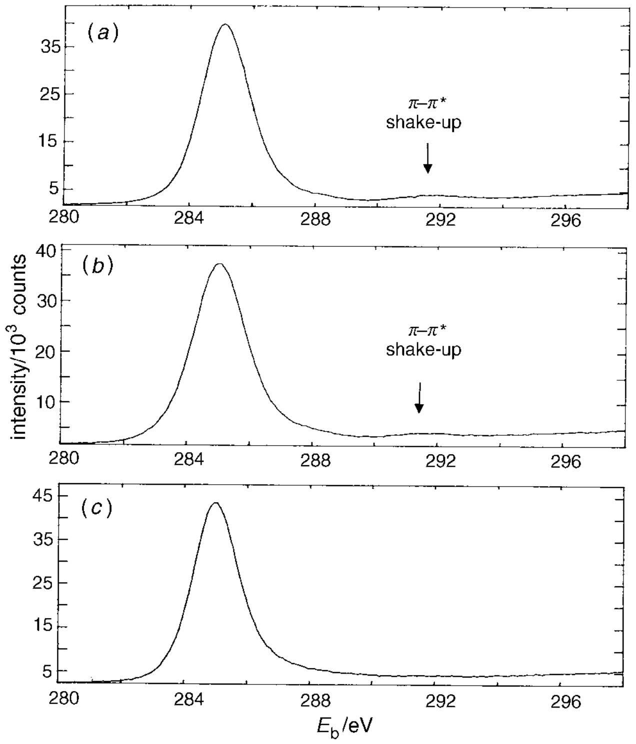

Fig. 3 High-resolution XPS spectra of the C 1s region: (*a*) an uncoated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex of 1.8 µm diameter; (*b*) and (*c*) polypyrrole-coated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latexes of 1.8 µm diameter with polypyrrole mass loadings of 1.0% and 8.9% respectively (see samples 4 and 1 in Table 1). Note that the π–π^* shake-up satellite at *ca.* 291.5–292.0 eV due to the aromatic rings in the underlying polystyrene latex is absent in spectrum (*c*). This is consistent with a thicker, more uniform polypyrrole overlayer.

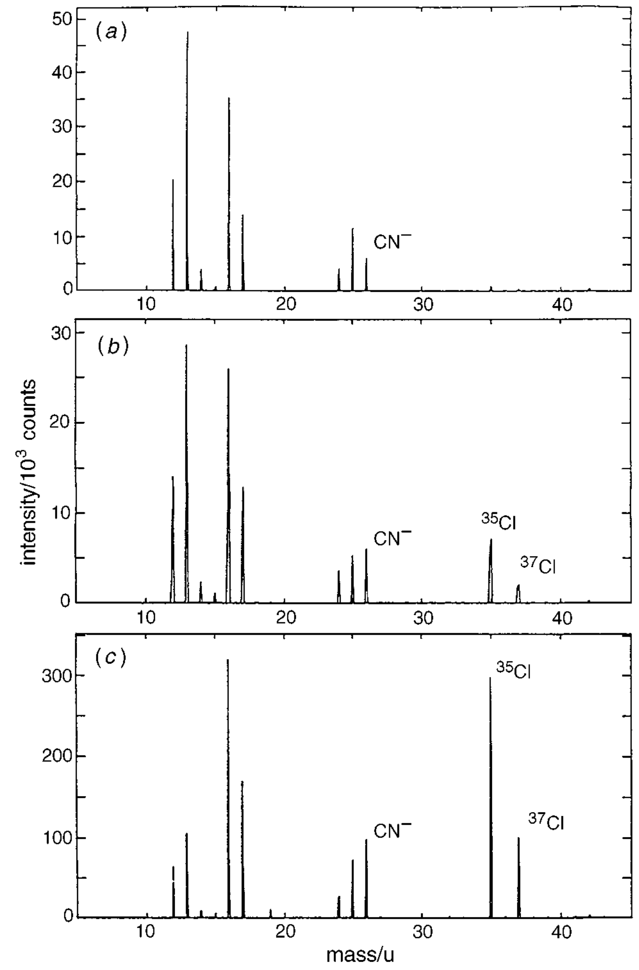

Fig. 4 Negative-ion TOF-SIMS spectra of: (*a*) an uncoated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex of 1.8 µm diameter; (*b*) polypyrrole chloride bulk powder prepared by conventional precipitation polymerization in the absence of any latex; and (*c*) a polypyrrole-coated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex of 1.8 µm diameter (8.9% polypyrrole mass loading; sample 1 in Table 1)

Raman spectroscopy

The Raman results are summarized in Fig. 5. The spectrum of an uncoated polystyrene latex is shown in Fig. 5(*d*). There are several strong signals which are characteristic of polystyrene at approximately 1002 cm^{-1} (ν_1 ring-breathing mode), 1603 cm^{-1} (ν_{9b} ring stretch), and 622 cm^{-1} (ν_{6b} ring deformation). This spectrum is in excellent agreement with the Raman spectra of polystyrene reported by previous workers.[15,16] A polypyrrole-coated polystyrene latex is shown in Fig. 5(*b*). The conducting polymer loading on this latex is only 1.0% by mass (N.B. essentially identical spectra were also obtained at polypyrrole loadings of 3.0 and 8.9%), yet this Raman spectrum is identical to that of pure polypyrrole.[17] Surprisingly, no signals attributable to polystyrene are

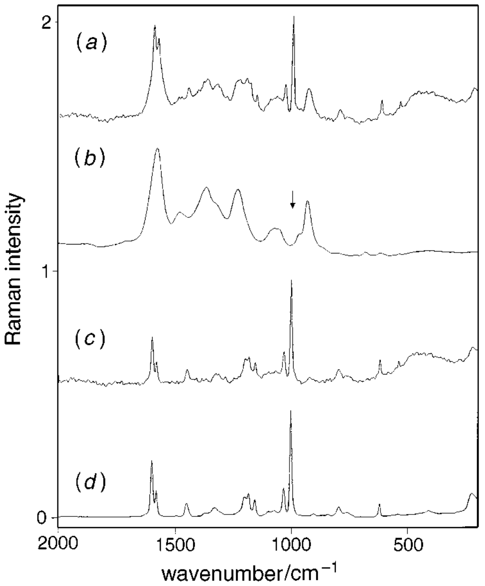

Fig. 5 Raman spectra of: (*a*) a heterogeneous mixture comprising 3% polypyrrole chloride bulk powder and 97% poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex; (*b*) a polypyrrole-coated, poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex with a polypyrrole mass loading of 1.0% (sample 4 in Table 1); (*c*) the difference spectrum obtained by subtracting spectrum (*b*) from spectrum (*a*); (*d*) an uncoated poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex. Note the strong polystyrene bands in spectrum (*a*); these features are not visible in spectrum (*b*).

observed, even though this relatively strong Raman scatterer has its strongest signal (1002 cm^{-1}) occurring in a region of near-baseline Raman intensity for polypyrrole. Why are there no Raman features attributable to polystyrene in a composite which contains 99% polystyrene by mass? This observation is believed to be directly related to the 'core–shell' particle morphology of the coated latexes. The polypyrrole overlayer must either completely absorb the Raman excitation light and/or attenuate the Raman signal arising from the underlying polystyrene latex. In this context it is worth emphasising that the excitation wavelength of 1064 nm is very near the strong, broad optical absorption band due to polypyrrole (λ_{max} *ca.* 950–1000 nm). We note that similar 'skin-effect' observations have been reported by other workers[18] in Raman studies of the surface chemistry of graphite or carbon fibres and, more importantly, by Hearn *et al.* for the Raman spectra of polypyrrole-coated polyester fibres.[19] However, it is remarkable that such efficient attenuation is observed in the present work since, at a conducting polymer mass loading of 1.0%, the thickness of the polypyrrole overlayer on the polystyrene latex particles is extremely thin (*ca.* 2 nm; see sample 4 in Table 1). In contrast, the conducting polymer overlayers on the polypyrrole-coated polyester fibres studied by Hearn *et al.* were much thicker (> 100 nm).[19]

In order to verify the unusual observations described above, control experiments were carried out using a heterogeneous admixture with a mass composition of 3% polypyrrole chloride 'bulk powder' and 97% uncoated polystyrene latex. The Raman spectrum of this admixture is shown in Fig. 5(*a*). There is no possibility of a 'core–shell' morphology for such an admixture and, as expected, the signals associated with the polystyrene latex are readily observed, even though this control sample has a slightly lower polystyrene content than the core–shell latex [Figure 5(*b*)]. Some polypyrrole bands are also apparent in Fig. 5(*a*) but these are much less intense than those observed in Fig. 5(*b*). Finally, spectrum (*b*) was subtracted from spectrum (*a*) to obtain a difference spectrum [Fig. 5(*c*)]. Although somewhat noisier, spectrum (*c*) is essentially identical to that of the uncoated polystyrene latex [Figure 5(*d*)]. Thus, in contrast to the coated latex, the two components in the heterogeneous admixture are essentially additive, as expected. We conclude that the 'core–shell' particle morphology of these polypyrrole-coated polystyrene latexes is responsible for the complete attenuation of the signal from the polystyrene core, even at a polypyrrole overlayer thickness of only 2 nm.

UV–VIS reflectance spectroscopy

During the course of the Raman control experiments described above, it was noted that the polypyrrole-coated polystyrene latexes were distinctly more coloured (*i.e.* appeared a darker shade of grey) than the corresponding heterogeneous admixtures of dried polypyrrole bulk powder and polystyrene latex with the same conducting polymer loadings. An attempt to quantify this observation was made using diffuse reflectance UV–VIS spectroscopy. The results are depicted in Fig. 6 for a polypyrrole-coated polystyrene latex with a polypyrrole mass loading of 4.6% (sample 3) and the equivalent heterogeneous admixture (polypyrrole mass loading 5.0%). It is clear that the coated latex has a significantly lower reflectance (*i.e.* higher absorbance), which is again consistent with the 'core–shell' particle morphology proposed for this material.

Scanning force microscopy

Our earlier studies[1,2] of polypyrrole-coated polystyrene particles using scanning electron microscopy suggested that the polypyrrole overlayer was remarkably smooth and uniform at polypyrrole loadings lower than approximately 10% by mass. However, these morphological studies were somewhat restricted by the relatively low SEM resolution. It is well known that scanning force microscopy (SFM) has a much higher resolution than SEM so it was decided to use this technique to study the nanomorphology of both the uncoated and coated polystyrene latexes. Fig. 7(*a*) shows an image of an isolated, uncoated 1.8 μm polystyrene latex. These particles have a relatively smooth, featureless morphology, with relatively few imperfections. In contrast, an image of a polypyrrole-coated polystyrene latex particle (1.0% polypyrrole loading by mass) is shown in Fig. 7(*b*). The nanomorphology of the polypyrrole overlayer is clearly somewhat rougher than that of the uncoated latex particles and appears to be composed of individual nanosized features of 10–20 nm. It is noteworthy that these features were not observed in our SEM studies,[2] presumably due to this

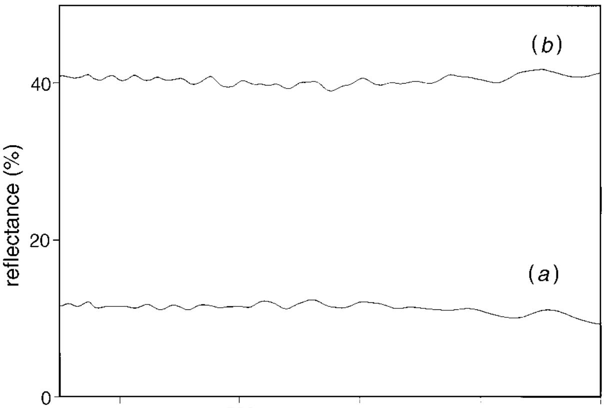

Fig. 6 UV–VIS reflectance spectra (obtained using a diffuse reflectance accessory) for (*a*) a polypyrrole-coated polystyrene latex (polypyrrole loading 4.6% by mass; sample 3 in Table 1) and (*b*) a heterogeneous admixture comprising 5% polypyrrole bulk powder and 95% polystyrene latex (1.8 μm diameter). The observed lower reflectance for the former spectrum indicates increased light absorption by the core–shell particles.

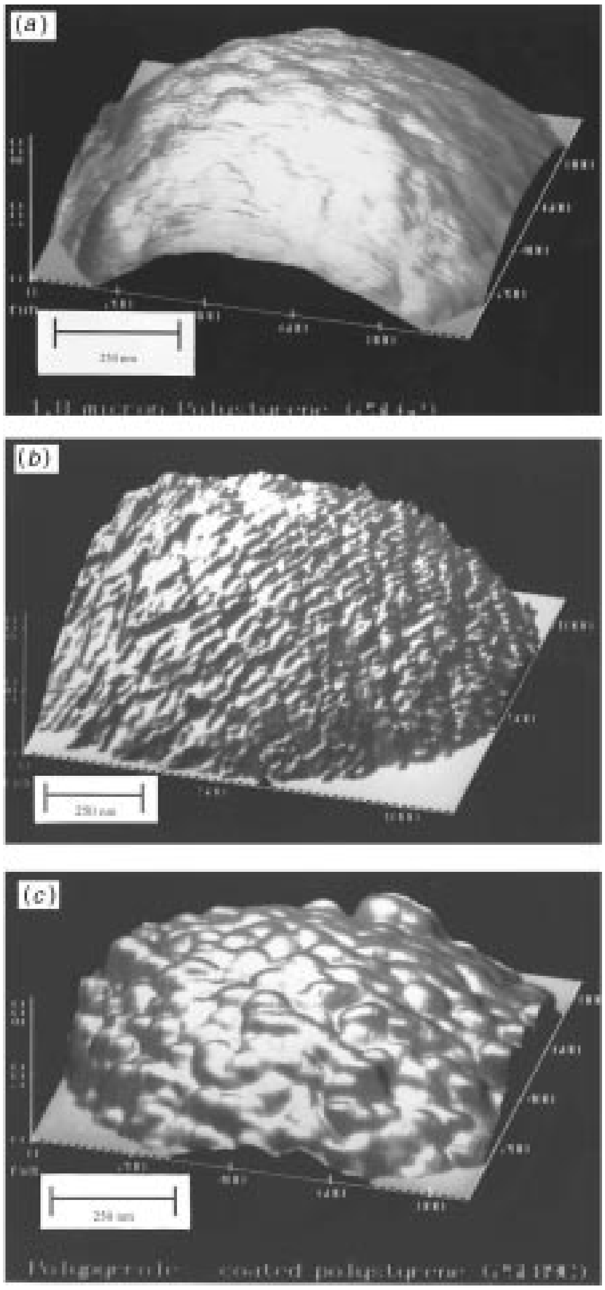

Fig. 7 SFM images of (*a*) an uncoated 1.8 µm diameter poly(*N*-vinylpyrrolidone)-stabilized polystyrene latex; (*b*) a polypyrrole-coated polystyrene latex with a polypyrrole mass loading of 1.0% (sample 4) and (*c*) a polypyrrole-coated polystyrene latex with a polypyrrole mass loading of 8.9% (sample 1)

latter technique's poorer resolution. On the other hand, similar nanomorphologies for polypyrrole overlayers on textile fibres (STM) were reported using scanning tunnelling microscopy (STM) in an earlier study.[20] An SFM image of a polypyrrole-coated polystyrene latex at a higher polypyrrole loading (8.9% by mass) is shown in Fig. 7(*c*). This thicker polypyrrole overlayer has a distinctly 'globular' morphology, with features of the order of 50 nm. These globular features were also observed in our earlier SEM studies[2] and are very similar to the morphology of relatively thick polypyrrole coatings on quartz fibres.[21] At least ten polypyrrole-coated latex particles were analyzed by SFM. In each case, the polypyrrole overlayers appear to be reasonably continuous, with little or no evidence of bare patches. This is consistent with both the Raman spectroscopy observations discussed above and also with a 'core–shell' particle morphology.

Scanning electron microscopy and IR spectroscopy studies

At this point in our investigation all the experimental evidence suggested a 'core–shell' morphology for the polypyrrole-coated polystyrene particles. We were aware that the Lehigh group had successfully used solvent extraction to examine the particle morphology of poly(methyl methacrylate)/polystyrene 'core–shell' latexes.[22] Since there is some literature evidence that polypyrrole is lightly cross-linked,[23] extraction of the uncross-linked polystyrene 'core' with a suitable organic solvent was attempted. If successful, the polypyrrole 'shells' should remain as insoluble residues. Accordingly, a dried polypyrrole-coated 1.6 µm polystyrene latex (6.5% polypyrrole loading by mass; sample 2 in Table 1) was treated with THF (see Experimental section). After isolation and drying, the mass loss was found to be consistent with quantitative extraction of the polystyrene component. Analysis of the black residues using FTIR spectroscopy confirmed that this material was essentially just polypyrrole (see Fig. 8), with very little evidence for the original polystyrene component (compare the relatively weak intensity of the band at 702 cm^{-1} with the corresponding very strong band observed in the IR spectrum of the polypyrrole-coated polystyrene latex). Examination of these polypyrrole residues by SEM revealed a 'broken egg-shell' morphology (see Fig. 9), with the 'egg-shell' diameter corresponding to that of the original coated particles. Thus, this solvent extraction experiment confirms beyond all reasonable doubt that these composite particles do indeed possess a 'core–shell' morphology. There are two possible explanations for the success of the extraction experiment: (1) the THF could permeate the continuous polypyrrole overlayer, causing the polystyrene core to swell and eventually leading to rupturing of the polypyrrole overlayer; (2) the polypyrrole overlayer is not completely continuous and the THF diffuses into the latex core *via* imperfections or defects in the polypyrrole overlayer. Finally, we note that the 'broken egg-shell' polypyrrole morphology is highly unusual and may be useful in catalysis applications. Thus, smaller polystyrene latex particles could possibly serve as a colloidal 'template' for the synthesis of high surface area polypyrroles with unusual morphologies.

Conclusions

Several micrometre-sized polypyrrole-coated polystyrene latexes have been characterized in terms of their surface

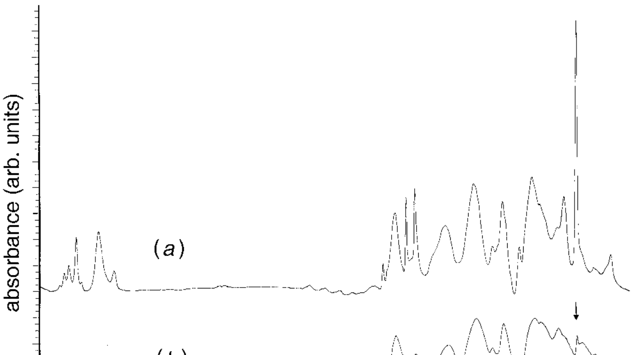

Fig. 8 FTIR spectra of (*a*) a polypyrrole-coated polystyrene latex (mass loading 6.5%; sample 2 in Table 1) and (*b*) the polypyrrole broken egg-shells residues remaining after solvent extraction of the polystyrene component using THF (a non-solvent for the polypyrrole component). The polystyrene bands are much weaker in the latter spectrum, thus confirming quantitative extraction of this component.

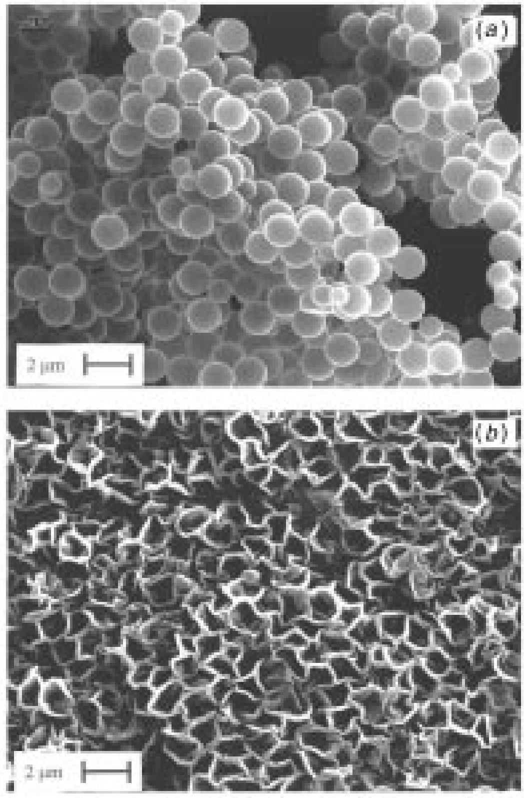

Fig. 9 Scanning electron micrographs of (*a*) a polypyrrole-coated polystyrene latex (mass loading 6.5%; sample 2) and (*b*) the resulting polypyrrole residues after solvent extraction of the underlying polystyrene core particles using THF (a non-solvent for the polypyrrole component). The broken egg-shells morphology clearly evident in the latter micrograph confirms the core–shell particle morphology of the original polypyrrole-coated latex particles.

composition and nanomorphology using a wide range of techniques. XPS and TOF-SIMS studies were consistent with a relatively uniform conducting polymer overlayer containing chloride dopant anions. XPS provided some evidence for the underlying polystyrene latex at lower polypyrrole loadings. Raman studies were also consistent with a core–shell particle morphology, since only vibrational bands due to polypyrrole were observed. Remarkably, no evidence was found for the underlying polystyrene component, even for polypyrrole overlayer thicknesses as low as 2 nm. This is attributed to unusually efficient attenuation of the polystyrene bands by the polypyrrole overlayer. The enhanced absorbance (reduced reflectance) of the polypyrrole-coated polystyrene latex particles relative to their corresponding heterogeneous admixtures was confirmed by UV–VIS reflectance spectroscopy. At low polypyrrole loadings (1.0 mass%) the nanomorphology of the conducting polymer overlayer was relatively smooth, but a rougher, more globular nanomorphology was observed using SFM at higher loadings (8.9 mass%). Solvent extraction of the underlying polystyrene latex core was quantitative and revealed a 'broken egg-shell' morphology for the polypyrrole residues, thus providing irrefutable evidence for a 'core–shell' particle morphology.

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References

1 S. F. Lascelles and S. P. Armes, *Adv. Mater.*, 1995, **7**, 864.

2 S. F. Lascelles and S. P. Armes, *J. Mater. Chem.*, preceding paper.

3 (*a*) A. R. Goodall, M. C. Wilkinson and J. Hearn, *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**, 2193; (*b*) C. W. A. Bromley, *Colloids Surf.*, 1986, **17**, 1.

4 (*a*) A. J. Paine, W. Luymes and J. McNulty, *Macromolecules*, 1990, **23**, 3104; (*b*); C. K. Ober, K. P. Lok and M. L. Hair, *J. Polym. Sci., Polym. Lett.*, 1985, **23**, 103.

5 H. Ge, P. R. Teasdale, G. G. Wallace, *J. Chromatogr.*, 1991, **544**, 305.

6 (*a*) H. Kawaguchi, *Microspheres for Diagnosis and Bioseparation* in *Polymer Materials for Bioanalysis and Bioseparation*, ed. T. Tsuruta *et al.*, CRC Press, London, 1993; (*b*) P. J. Tarcha, D. Misun, M. Wong and J. J. Donovan, *Polymer Latexes*: *Preparation, Characterisation and Applications*, ed. E. S. Daniels, E. D. Sudol and M. S. El-Aassar, *ACS. Symp. Ser. no. 492*, 1992, **22**, 347; (*c*) M. R. Pope, S. P. Armes and P. J. Tarcha, *Bioconjugate Chem.* 1996, **7**, 436.

7 D. B. Cairns, S. P. Armes, M. M. Chehimi, M. Delamar and S. Y. Luk, *Macromolecules*, to be submitted.

8 (*a*) A. E. Wiersma and L. M. A. vd Steeg, *Eur. Pat.*, 589 529; (*b*) A. E. Wiersma, L. M. A. vd Steeg and T. J. M. Jongeling, *Synth. Met.*, 1995, **71**, 2269.

9 C. Perruchot, M. M. Chehimi, M. Delamar, S. F. Lascelles and S. P. Armes, *Langmuir*, 1996, **12**, 3245.

10 J. C. Vickerman, A. Brown and N. M. Reed, *Secondary Ion Mass Spectrometry*: *Principles and Applications*, Clarendon Press, Oxford, 1989.

11 B. Drake, C. B. Prater, A. L. Weisenhorn, S. A. C. Gould, T. R. Albrecht, C. F. Quate, D. S. Cannell, H. G. Hansma, and P. K. Hansma, *Science*, 1989, **243**, 1586.

12 Y. Deslandes, D. F. Mitchell and A. J. Paine, *Langmuir*, 1993, **9**, 1468.

13 (*a*) M. M. Chehimi, S. F. Lascelles and S. P. Armes, *Chromatographia*, 1995, **41**, 671; (*b*) M. M. Chehimi, M. L. Abel, Z. Sahraoui, K. Fraoua, S. F. Lascelles and S. P. Armes, *Int. J. Adhes. Adhes.*, 1997, **17**, 1.

14 (*a*) M. L. Abel, S. R. Leadley, A. M. Brown, J. Petitjean, M. M. Chehimi and J. F. Watts, *Synth. Met.*, 1994, **66**, 85; (*b*) S. Y. Luk, W. Lineton, M. Keane, C. DeArmitt and S. P. Armes, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 905.

15 R. S. Venkatachalam, F. J. Boerio, P. G. Roth and W. H. Tsai, *J. Polym. Sci., Part B: Polym. Phys.* 1988, **26**, 2447.

16 (*a*) C. H. Jones and I. J. Wesley, *Spectrochim. Acta, Part A*, 1991, **47**, 1293; (*b*) R. A. Nyquist, C. L. Putzig, M. A. Leugers, R. D. McLachlan and B. Thill, *Appl. Spectrosc.*, 1992, **46**, 981.

17 C. M. Jenden, R. G. Davidson and T. G. Turner, *Polymer*, 1993, **34**, 1649.

18 (*a*) F. Tuinstra and J. L. Koenig, *J. Chem. Phys.*, 1970, **53**, 1126; (*b*) M. A. Tadayyoni and N. R. Dando, *Appl. Spectrosc.*, 1991, **45**, 1613.

19 M. J. Hearn, I. W. Fletcher, S. P. Church and S. P. Armes, *Polymer*, 1993, **34**, 262.

20 S. P. Armes, M. Aldissi, M. Hawley, J. G. Beery and S. Gottesfeld, *Langmuir*, 1991, **7**, 1447.

21 S. P. Armes, S. Gottesfeld, J. G. Beery, F. Garzon, M. Mombourquette, M. Hawley and H. H. Kuhn, *J. Mater. Chem.*, 1991, **1**, 525.

22 S. Shen, M. S. El-Aasser, V. L. Dimonie, J. W. Vanderhoff and E. D. Sudol, *J. Polym. Chem., Part A*: *Polym. Chem.*, 1991, **29**, 857.

23 F. P. Bradner, J. S. Shapiro, H. J. Bowley, D. L. Gerrard and W. F. Maddams, *Polymer*, 1989, **30**, 914.

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