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Surface characterization of colloidal polypyrrole particles synthesized with reactive steric stabilizers using X-ray photoelectron spectroscopy

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X-ray photoelectron spectroscopy has been used to characterize the surfaces of polypyrrole colloids synthesized using reactive steric stabilizers based on statistical copolymers of 2-(dimethylamino)ethyl methacrylate. Three different copolymer stabilizers, containing 2-vinylpyrrole, 3-vinylthiophene and 2,2′-bithiophene-5-methyl methacrylate graft sites respectively, were examined. In each case, the grafted copolymer stabilizer was detected at the surface of the polypyrrole particles, which is consistent with the accepted steric stabilization mechanism of colloid stability. With the bithiophene-based copolymer stabilizer, the sulfur atoms in the bithiophene groups acted as unique elemental markers, and thus aided the detection and quantification of the stabilizer component. The atomic ratio of nitrogen to sulfur as determined by X.p.s. for this polypyrrole colloid was significantly higher than that observed for the corresponding copolymer stabilizer. This excess surface nitrogen was attributed to the polypyrrole component and is consistent with the relatively high solid-state conductivity (*ca.* 10^{-1} to $10^{0}\,\mathrm{S\,cm^{-1}}$) measured on compressed pellets of this dried colloid. The presence of the other two copolymer stabilizers at the surface of the polypyrrole particles is less obvious but can be verified from close inspection and comparison of the C_{1s} and N_{1s} core-line spectra of the two polypyrrole colloids, their corresponding copolymer stabilizers and a polypyrrole 'bulk powder' control sample respectively. Crown copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: polypyrrole; X-ray photoelectron spectroscopy; steric stabilization)

INTRODUCTION

Over the last two decades X-ray photoelectron spectroscopy (X.p.s.) has become a well-established technique for the surface characterization of organic polymers[1,2]. In the last ten years or so there has been increasing interest in using X.p.s. to examine polymer latex particles. Deslandes *et al.* have examined micron-sized polystyrene latexes stabilized with an adsorbed layer of poly(*N*-vinyl pyrrolidone)[3], whilst Davies and co-workers have published a series of papers [4-8] on the characterization of various sub-micron latexes using X.p.s. and secondary ion mass spectroscopy (SIMS). Generally it is found that the surface composition of the latex particles is consistent with the currently accepted steric and/or charge stabilization mechanisms for colloid stability[9,10].

There have been many reports describing the use of X.p.s. for the characterization of organic conducting polymers such as polypyrrole or polyaniline[11-19]. However, such studies have focused almost exclusively on chemically-synthesized powders or electrochemically-synthesized thin films. Since 1986 there have been numerous publications describing the synthesis of sterically stabilized polypyrrole particles via dispersion polymerization, usually in aqueous media[20-25]. These colloidal dispersions are significantly more processable than conventional polypyrrole, which is a rather intractable material. The various polymeric stabilizers used to prevent macroscopic precipitation have generally been commercially available, e.g. cellulosic derivatives, poly(vinyl alcohol), poly(*N*-vinyl pyrrolidone) or poly(ethylene oxide); relatively few attempts have been made to design 'tailor-made' stabilizers[26,27]. In all cases the stabilizer is merely physically adsorbed onto the surface of the polypyrrole particles. In contrast, a wide

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range of *reactive* copolymer stabilizers (usually containing pendant aniline groups) have been reported for the preparation of polyaniline colloids[28–32]. Recently, the Sussex group has described the analogous synthesis of polypyrrole particles using 'tailor-made' reactive copolymer stabilizers based on poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA)[33]. Successful grafting was achieved by incorporating reactive pyrrolic, or (bi)thiophene groups into the water-soluble PDMAEMA backbone via statistical copolymerization of DMAEMA with appropriate vinyl comonomers such as 2-vinylpyrrole or 3-vinylthiophene.

In principle, this 'reactive stabilizer' approach should allow polypyrrole colloids to be synthesized using polymeric stabilizers based on a much wider range of comonomers than is presently used [e.g. (meth)acrylamide, 4-styrenesulfonic acid, (meth)acrylic acid etc.]. Potential applications for such dispersions include their use as novel 'marker' particles for immunodiagnostic assays[34,35]. Here the ability to incorporate functionality into the tailor-made stabilizers (e.g. amine or carboxylic acid groups as specific binding sites for the biological molecules of interest) is likely to be beneficial in minimizing the ubiquitous non-specific binding effects which normally plague such assays. Furthermore, chemical grafting of the functional steric stabilizer onto the surface of the polypyrrole particles should lead to more robust assays. In the present work we have utilized X.p.s. to characterize the surfaces of polypyrrole colloids synthesized using three different graft copolymer stabilizers. The aim was to verify that the grafted copolymer stabilizers are indeed located at the surface of the polypyrrole particles.

EXPERIMENTAL

Copolymer stabilizer synthesis

The copolymer stabilizers were synthesized via the conventional free-radical statistical copolymerization of DMAEMA with either 2-vinylpyrrole (2-VPY), 3-vinylthiophene (3-VT) or 2,2'-bithiophene-5-methyl methacrylate (BTMA) comonomers using AIBN in toluene at 70°C as described previously[33]. The initial comonomer feed ratio was typically 10 : 1 in favour of the DMAEMA comonomer. The resulting copolymers were purified by precipitation into *n*-hexane. Copolymer composition was assessed using ^{1}H n.m.r. spectroscopy: the three copolymer stabilizers contained approx. 7 mol% BTMA, 11 mol% 3VT and 15 mol% 2VPY respectively (see *Figure 1*). Analysis of stabilizer molecular weights using gel permeation chromatography indicated polydispersities (M_w/M_n) of 2.2–2.6 and M_n values of 18 000–26 000 (PMMA standards, THF eluent, RI detector).

Colloid synthesis and characterization

The polypyrrole colloids were synthesized as follows (see *Figure 2*): pyrrole (1.00 ml) was added to an aged (0–30 min at room temperature), stirred aqueous solution (100 ml) containing the copolymer stabilizer (1.00 g) and $FeCl_3$ oxidant (5.80 g). The solution turned black within a few seconds and was stirred at room temperature for at least 16 h. The resulting black dispersion was centrifuged at 40 000 rpm for 1–2 h, the coloured supernatant was carefully decanted, and the black sediment

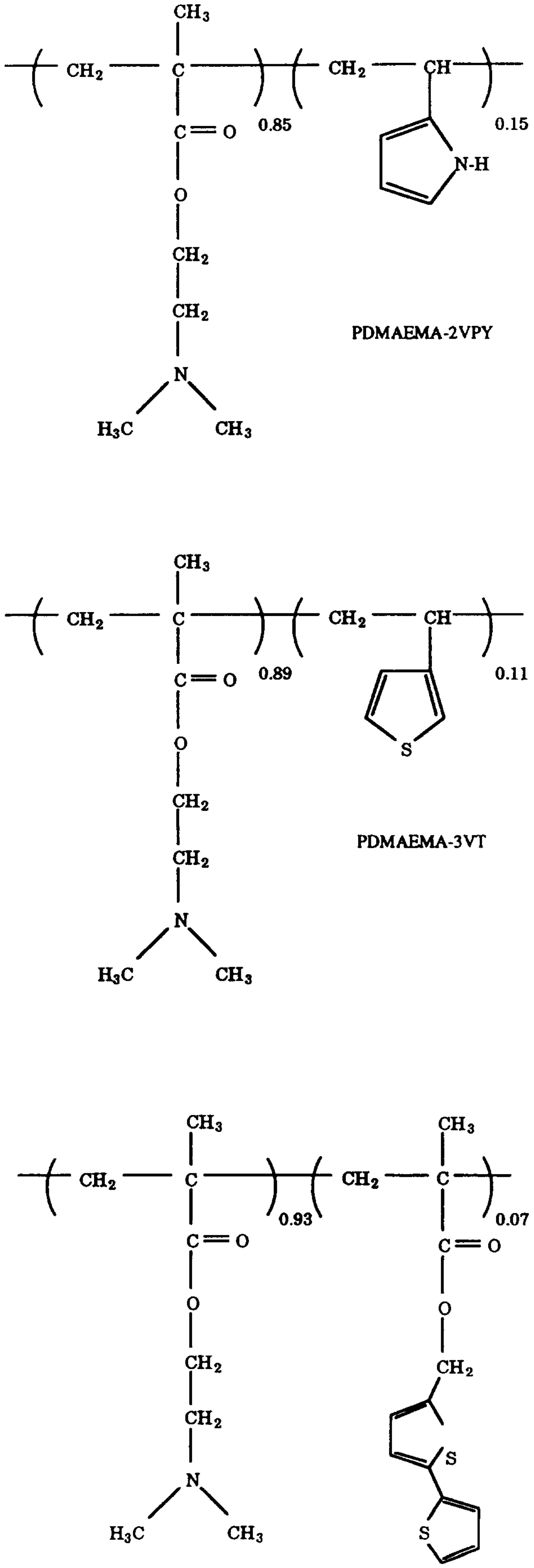

Figure 1 Chemical structures of the three reactive copolymer stabilizers as determined by ^{1}H n.m.r. spectroscopy

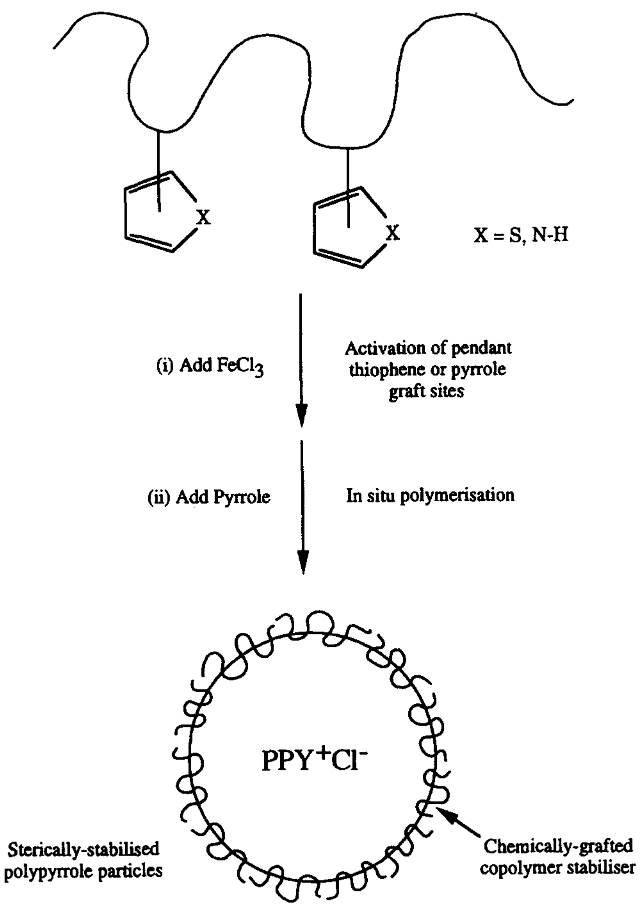

Figure 2 Schematic representation of the synthesis of polypyrrole colloids via aqueous dispersion polymerization using statistical copolymer stabilizers which contain reactive pyrrolic or (bi)thiopene groups

was redispersed in water using an ultrasonic bath. This centrifugation–redispersion cycle was repeated twice to ensure the complete removal of inorganic by-products and excess, non-grafted copolymer stabilizer. Colloid powders were obtained by evaporation in a 70°C oven overnight. Conventional four-point probe conductivity measurements were carried out on 13 mm diameter compressed pellets at room temperature.

X-ray photoelectron spectroscopy studies

For the X.p.s. measurements, the polymer films were mounted on standard sample studs by means of double-sided adhesive tape. Core-line spectra (average of 2–12 scans depending on the element) and wide-scan spectra (1 scan) were obtained on a VG ESCALAB MkII spectrometer using MgKα radiation (1253.6 eV photons) at a constant retard ratio of 40 using a take-off angle (α) of 75° (measured with respect to the sample surface). To minimize radiation damage to the polymer films, the X-ray source was operated at a reduced power of 120 W (12 kV and 10 mA). Throughout the measurements, the pressure in the analysis chamber was maintained at 10^{-8} mbar or lower. To compensate for surface charging effects, all binding energies were referenced to the C_{1s} neutral carbon peak at 284.6 eV. Surface chemical compositions were determined from peak-area ratios, corrected with appropriate experimentally determined sensitivity factors, and were liable to a ±10% error.

RESULTS AND DISCUSSION

Recently the Sussex group have shown that X.p.s. can be used to examine the surface composition of both polypyrrole–silica and polyaniline–silica nanocomposites[36] and also poly(potassium 3-sulfopropylmethacrylate)-stabilized polypyrrole particles[37]. Interpretation and analysis of the X.p.s. data is straightforward if the conducting polymer and the dispersant (polyelectrolyte or silica) components contain unique elemental markers (e.g. nitrogen for the conducting polymer and silicon or sulfur for the silica or polyelectrolyte dispersant). However, difficulties are encountered if one of the elemental markers is not unique. For example, for polypyrrole particles doped with sulfate anions and stabilized with sodium dodecylbenzenesulfonate surfactant, the sulfur marker is present in both the conducting polymer and the dispersant components. In such cases the information which can be obtained is more limited[38].

In the present study two of the three reactive copolymer stabilizers (PDMAEMA-3VT and PDMAEMA-BTMA) contained sulfur due to their (bi)thiophene graft sites. Since each polypyrrole colloid was synthesized using the FeCl$_3$ oxidant, the polypyrrole component contained no sulfur [in contrast, polypyrrole synthesized using the $(NH_4)_2S_2O_8$ oxidant contains sulfur atoms in the form of SO_4^{2-} or HSO_4^- dopant anions]. Thus sulfur can, in principle, act as a unique elemental marker for these two copolymer stabilizers in the surface characterization of the colloid samples by X.p.s. On the other hand, the PDMAEMA-2VPY stabilizer contains no unique elemental markers compared with polypyrrole. Thus detection of this latter stabilizer at the surface of the polypyrrole particles was expected to be more problematic.

Each of the three reactive copolymers, PDMAEMA-BTMA, PDMAEMA-3VT and PDMAEMA-2VPY proved to be effective steric stabilizers for polypyrrole. The particle size of the polypyrrole colloids was determined to be approx. 100 nm by transmission electron microscopy in each case[33]. Our earlier i.r. spectroscopic studies on the dried colloids (KBr disc) revealed strong polypyrrole signatures, with an additional small carbonyl peak at *ca.* 1720 cm^{-1} due to the ester carbonyl group of the DMAEMA-based copolymer stabilizer[33]. These i.r. data confirmed that the stabilizers were indeed incorporated into the polypyrrole particles. However, since i.r. spectroscopy is a 'bulk' technique, the location of the stabilizer could not be established.

A summary of the X.p.s. surface chemical compositions of the three copolymer stabilizers, the three polypyrrole colloids synthesized using these stabilizers and a polypyrrole 'bulk powder' control sample is presented in *Table 1*. Interpretation of the X.p.s. data obtained for each of the three colloid systems is considered in turn below:

(1) PDMAEMA-BTMA stabilized polypyrrole colloid

Figure 3 shows the X.p.s. wide scan spectra obtained for this polypyrrole colloid, its copolymer stabilizer and a polypyrrole 'bulk powder' control sample. As expected, there is a sulfur signal at *ca.* 164.1 eV due to the bithiophene groups in the copolymer stabilizer spectrum. This sulfur signal is noticeably weaker, but nevertheless visible, in the colloid spectrum. X.p.s. is a

Table 1 X.p.s. surface compositional data for the three reactive copolymer stabilizers, the three corresponding polypyrrole colloids synthesized using these stabilizers and the polypyrrole 'bulk powder' synthesized in the absence of stabilizer using $FeCl_3$ oxidant

Sample description	C/N ratio	N/S ratio	Cl/N ratio	Conductivity[a] (S cm^{-1})
PPY 'bulk powder' control sample	5.0	–	0.32	5.0
PDMAEMA-BTMA stabilizer	11.9	5.0		$< 10^{-6}$
PDMAEMA-3VT stabilizer	12.5	7.1		$< 10^{-6}$
PDMAEMA-2VPY stabilizer	11.3	–		$< 10^{-6}$
PDMAEMA-BTMA PPY colloid	6.4	14.3	0.43	1.5
PDMAEMA-3VT PPY colloid	5.0	100	0.33	3.5
PDMAEMA-2VPY PPY colloid	6.8	–	0.33	0.1

[a] Measured on compressed pellets of the dried powders using the conventional four-point probe method

highly surface-specific technique, with a typical sampling depth of only 1–5 nm. Thus the presence of this particular stabilizer at (or very near) the surface of the polypyrrole particles is confirmed unambiguously. The N/S atomic ratios calculated from the X.p.s. spectra are 5.0 and 14.3 for the stabilizer and colloid respectively (see *Table 1*). The relative increase in the surface nitrogen content of the colloid suggests that the PDMAEMA-BTMA stabilizer does not completely cover the surface of the polypyrrole particles in the solid state. A similar 'patchy' stabilizer layer model has been suggested by Deslandes *et al.* for poly(*N*-vinyl pyrrolidone)-stabilized polystyrene particles[3] and by Armes and co-workers for both surfactant-stabilized and polyelectrolyte-stabilized polypyrrole particles[37,38]. On the basis of the above N/S ratios, we estimate that the surface coverage of the polypyrrole particles by the PDMAEMA-BTMA stabilizer is only *ca.* 35%. Further evidence for the co-existence of polypyrrole and stabilizer at the particle surface can be found in the C/N atomic ratios of *Table 1*. The surface C/N ratio of the polypyrrole 'bulk powder' is 5.0, whereas the PDMAEMA-BTMA stabilizer has a surface C/N ratio of 11.9. The surface C/N ratio of the colloid is intermediate between these two values at 6.4. However, we wish to emphasize that all three copolymer stabilizer samples were heavily contaminated with siloxane impurities (see *Figure 3a*, for example) which were inadvertently introduced during sample drying and/or mounting. Since these impurities also contain carbon, the C/N ratios calculated for the three copolymer stabilizers are likely to be over-estimates of the actual ratios (in contrast, the X.p.s. wide scan spectra of the three colloids and the polypyrrole 'bulk powder' sample are essentially free of contamination). Thus conclusions based on calculated C/N ratios are likely to be much less reliable than those based on N/S ratios.

Returning to the colloid wide scan spectrum in *Figure 3b*, a prominent peak attributable to chlorine is observed at *ca.* 198.0 eV. At first sight this must be due to the chloride dopant anions associated with the cationic polypyrrole chains. If this assignment is correct, the chlorine peak could, in principle, be used as a unique elemental marker for the conducting polymer component.

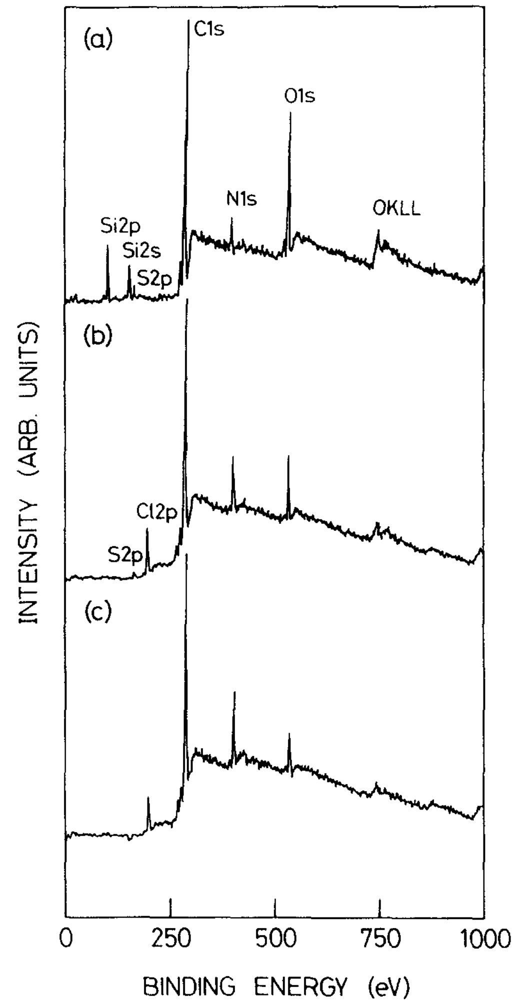

Figure 3 X.p.s. wide scan spectra for (a) the 'as-synthesized' PDMAEMA-BTMA copolymer stabilizer; (b) the polypyrrole colloid synthesized using this stabilizer; and (c) polypyrrole 'bulk powder' prepared in the absence of steric stabilizer

However, since a significant amount of HCl is generated during the pyrrole polymerization (the reaction solution has a final pH of 1–2 in a typical colloid synthesis), it is highly likely that the grafted DMAEMA-based copolymer stabilizer is converted into its amine hydrochloride form at the surface of the polypyrrole particles. There is some evidence of this in *Table 1*: the surface Cl/N ratio for this colloid is 0.43, which is considerably higher than that expected for doped polypyrrole (see 'bulk powder' control sample in *Table 1*). We note that the presence of the nitrogen-containing PDMAEMA-BTMA stabilizer at the particle surface would be expected to lead to a decrease in the Cl/N ratio, rather than the observed increase. Thus we believe that the anomalously high Cl/N ratio is best explained by the conversion of a significant proportion of the neutral amine groups in the PDMAEMA-BTMA stabilizer to their corresponding amine hydrochloride salts. Since all three colloids were synthesized using PDMAEMA-based stabilizers we conclude that chlorine is not a reliable elemental marker for polypyrrole in this study.

Finally, the C_{1s} and N_{1s} core-line spectra for the PDMAEMA-BTMA stabilizer, the colloid and the polypyrrole 'bulk powder' are shown in *Figure 4*. As expected, the C_{1s} core-line spectrum of the polypyrrole 'bulk powder' has a broad, relatively featureless

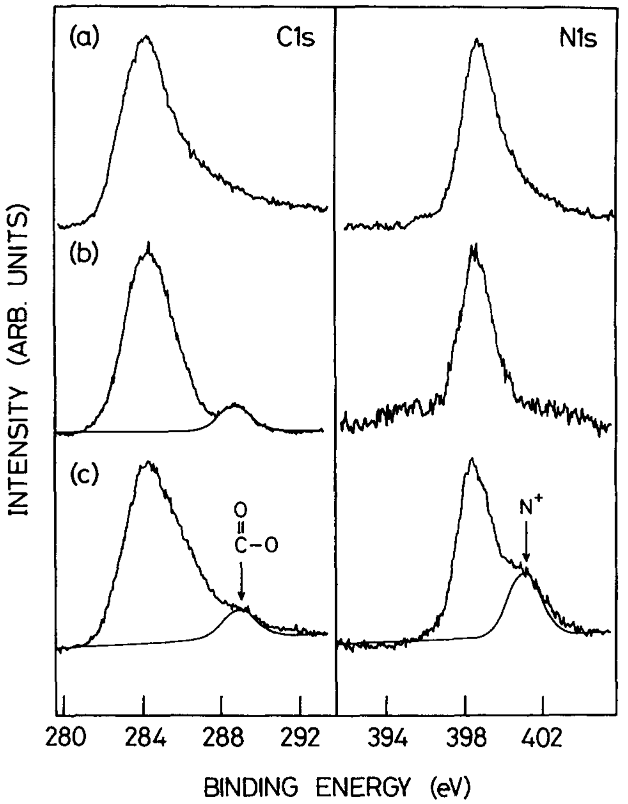

Figure 4 Core-line C_{1s} and N_{1s} X.p.s. spectra for (a) polypyrrole 'bulk powder' prepared in the absence of steric stabilizer; (b) 'as-synthesized' PDMAEMA-BTMA copolymer stabilizer; and (c) the polypyrrole colloid synthesized using this copolymer stabilizer

envelope[19]. In contrast, the C_{1s} spectrum of the PDMAEMA-BTMA stabilizer has a distinctive shoulder at 288.4 eV attributable to the ester carbonyl carbon of the DMAEMA comonomer. A similar shoulder is also discernible, albeit weaker, in the C_{1s} spectrum of the polypyrrole colloid. In the corresponding N_{1s} spectra, the signal due to the PDMAEMA-BTMA stabilizer is relatively narrow and symmetric whilst the polypyrrole 'bulk powder' signal is rather asymmetric. The high energy 'tail' in the latter spectrum has been previously assigned to imine nitrogen species (N^+) in the cationic polypyrrole chains[17,19]. This feature is much more prominent in the colloid spectrum, which has a distinct shoulder at 401.5 eV. This increase in N^+ species for the colloid is interpreted as further evidence for the conversion of neutral amine groups to amine hydrochloride sales in the PDMAEMA-BTMA stabilizer, and is consistent with the increased Cl/N ratio in the colloid noted above. Thus close inspection of the C_{1s} and N_{1s} spectra in *Figure 4* provides further evidence for the presence of the PDMAEMA-BTMA stabilizer adsorbed at the surface of the polypyrrole particles.

(2) PDMAEMA-3VT stabilized polypyrrole colloid

The PDMAEMA-3VT stabilizer also contains sulfur atoms (in its 3-vinylthiophene graft sites) which in principle could serve as a suitable elemental marker for this component. However, as *Figure 5* clearly shows, the S_{2p} signal in the corresponding colloid spectrum is barely above background noise (cf. the rather larger S_{2p} signal obtained for the PDMAEMA-BTMA-stabilized polypyrrole colloid). There is only one sulfur atom per 3-vinylthiophene graft site in the PDMAEMA-3VT stabilizer compared with two sulfur atoms per bithiophene-5-methyl methacrylate graft site for the PDMAEMA-BTMA stabilizer, so a reduced signal for the former stabilizer would be expected at any given surface concentration. On the other hand, the weak sulfur signal in the colloid spectrum may simply reflect a lower surface concentration of the PDMAEMA-3VT stabilizer; considered in isolation it does not represent particularly compelling evidence for the presence of this component. If we consider the C/N and Cl/N ratios of the colloid (see *Table 1*) these values are very similar to those of the polypyrrole 'bulk powder'. This observation is consistent with a relatively low surface concentration for the PDMAEMA-3VT stabilizer.

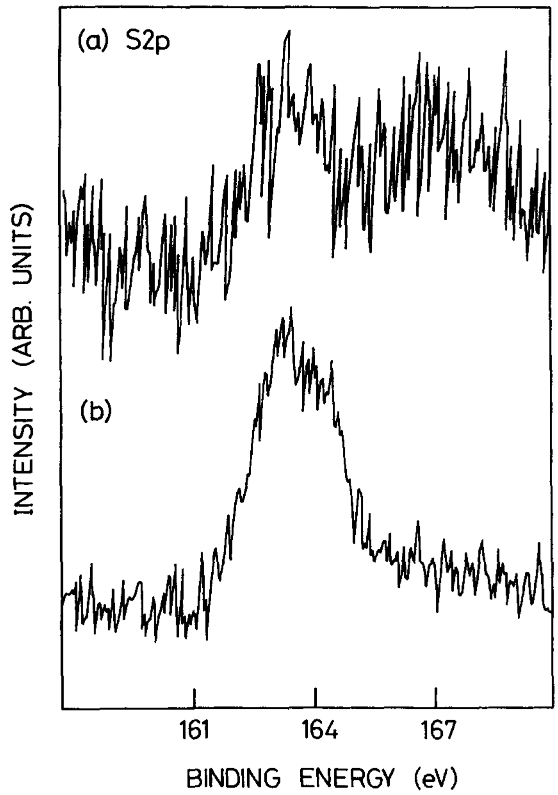

Figure 5. Core-line S_{2p} spectra for the two polypyrrole colloids synthesized using (a) the PDMAEMA-3VT and (b) the PDMAEMA-BTMA copolymer stabilizer respectively

Figure 6 shows the C_{1s} and N_{1s} core-line spectra for the colloid, the PDMAEMA-3VT stabilizer and the polypyrrole 'bulk powder' control sample. Again, the carbonyl ester carbon shoulder at 288.4 eV in the PDMAEMA-3VT stabilizer spectrum is also visible as a weak feature in the colloid spectrum. Similarly, the N^+ shoulder in the colloid is significantly more prominent than that found in the polypyrrole 'bulk powder' spectrum. Thus, in spite of its weak sulfur signal, we conclude that the PDMAEMA-3VT stabilizer, like the PDMAEMA-BTMA stabilizer, is located at the surface of the polypyrrole particles and that a significant proportion of the DMAEMA groups are present in their amine hydrochloride salt form.

(3) PDMAEMA-2VPY stabilized polypyrrole colloid

Detection of the PDMAEMA-2VPY stabilizer by X.p.s. was expected to be rather difficult since its elemental composition is very similar to that of polypyrrole. Admittedly it does not contain chlorine in

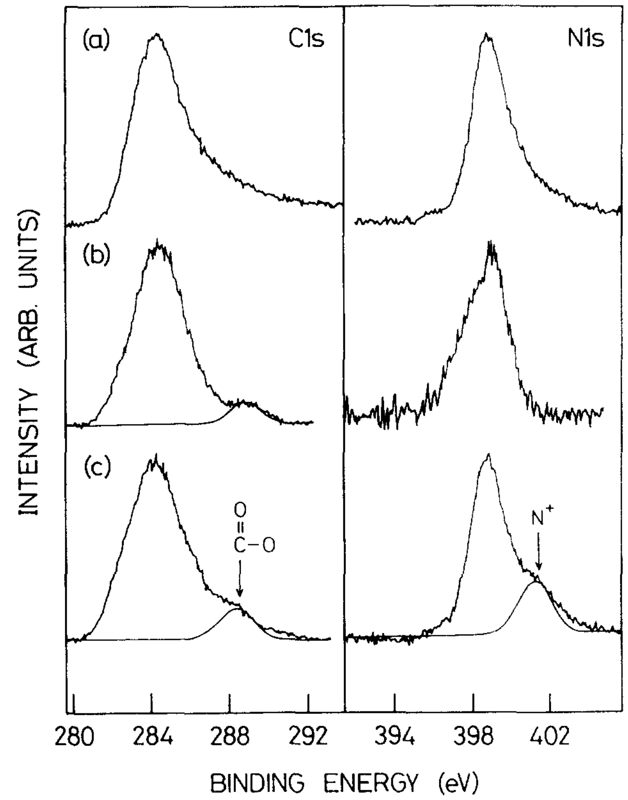

Figure 6 Core-line C_{1s} and N_{1s} X.p.s. spectra for (a) polypyrrole 'bulk powder' prepared in the absence of steric stabilizer; (b) 'as-synthesized' PDMAEMA-3VT copolymer stabilizer; and (c) the polypyrrole colloid synthesized using this copolymer stabilizer

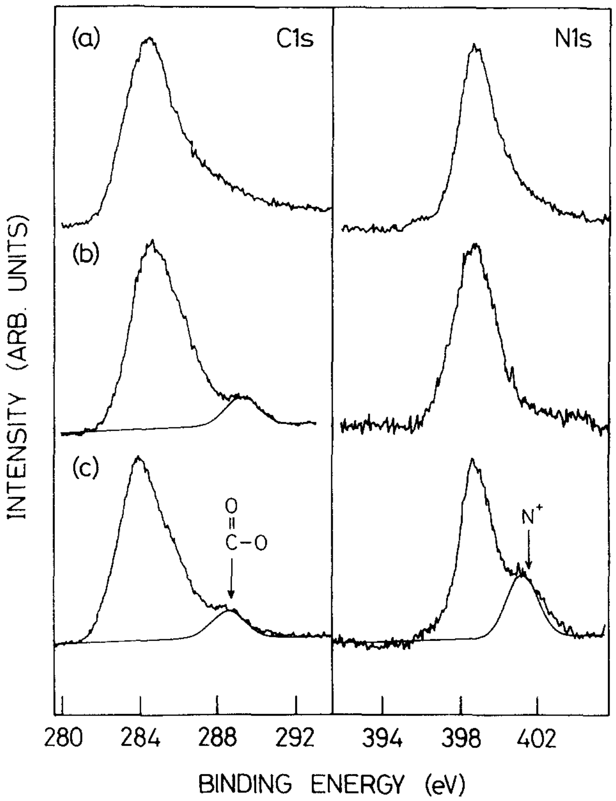

Figure 7 Core-line C_{1s} and N_{1s} X.p.s. spectra for (a) polypyrrole 'bulk powder' prepared in the absence of steric stabilizer; (b) 'as-synthesized' PDMAEMA-2VPY copolymer stabilizer; and (c) the polypyrrole colloid synthesized using this copolymer stabilizer

its as-synthesized form (see *Figure 1*) but, as we have seen with the two (bi)thiophene-based stabilizers discussed above, it is very likely that at least some of the DMAEMA groups on the grafted PDMAEMA-2VPY stabilizer are present in their amine hydrochloride salt form. Thus the best evidence for the presence of the grafted stabilizer was likely to be found in the C_{1s} and N_{1s} core-line spectra of the colloid. These spectra are presented in *Figure 7*. As expected, a weak shoulder attributable to ester carbonyl carbon is visible at 288.4 eV in the C_{1s} spectrum of the colloid which corresponds to the slightly more prominent shoulder observed in the C_{1s} spectrum of the stabilizer. Similarly, the N^+ shoulder at 401.5 eV in the colloid spectrum attributable to the protonated nitrogen of the DMAEMA hydrochloride salt is significantly more prominent than that observed for polypyrrole 'bulk powder' due to imine nitrogen. Taken alone, these observations only suggest, rather than confirm, the presence of the PDMAEMA-2VPY stabilizer. However, when considered in the light of the analogous results obtained on the polypyrrole colloids synthesized using the PDMAEMA-BTMA and PDMAEMA-3VT stabilizers, it seems reasonable to conclude that the PDMAEMA-2VPY stabilizer is also grafted onto the outside of the polypyrrole particles.

Finally, we note that the relatively high N/S ratios (see *Table 1*) found for the two (bi)thiophene-containing stabilizers provide some evidence for the presence of the conducting polymer component at the particle surface. Thus there is the possibility of direct electrical contact between adjacent polypyrrole particles in the solid state; this is consistent with the relatively high electrical conductivities measured on compressed pellets of these dried colloids (see last column of *Table 1*).

CONCLUSIONS

Our X-ray photoelectron spectroscopy studies have confirmed unequivocally that the PDMAEMA-BTMA stabilizer is present at the surface of the polypyrrole particles, since the sulfur atoms in the bithiophene graft sites of this stabilizer act as a unique elemental marker. The presence of the PDMAEMA-3VT and PDMAEMA-2VPY stabilizers is more difficult to verify but is apparent on close inspection of the C_{1s} and N_{1s} core-line spectra of the polypyrrole colloids, and comparison of these spectra with appropriate control samples. In all three colloids the weakly basic DMAEMA groups of the grafted stabilizers are at least partially converted to their amine hydrochloride salt form due to the *in situ* generation of HCl during the course of the pyrrole polymerization. The location of the stabilizer at the surface of all three colloids is consistent with the well-known steric stabilization mechanism of colloid stability. More importantly, our X.p.s. studies suggest that polypyrrole particles synthesized using similar reactive copolymer stabilizers containing carboxylic acid or amine functional groups should be useful in designing improved immunodiagnostic assays. Finally, for the two colloids synthesized using the (bi)thiophene-based stabilizers there is some evidence for the polypyrrole component at the particle surface. Thus, there is the possibility of direct contact between adjacent polypyrrole particles in the solid state; this is consistent with the relatively high electrical conductivities measured for these samples.

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