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Synthesis and Characterisation of Sterically-stabilised Polypyrrole Particles Using a Chemically Reactive Poly(vinyl amine)-based Stabiliser

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ABSTRACT. Poly(vinyl amine) (PVAm) was derivatised using 2-thiophenecarboxaldehyde via Michael addition to prepare a statistical copolymer stabiliser for the synthesis of primary amine-functionalised polypyrrole (PPy) particles. A minimum stabiliser concentration of around 20 w/v % relative to pyrrole was required for well-defined PPy particles of approximately 100-200 nm, as judged by TEM and DLS. FT-IR spectroscopy confirmed that stabiliser grafting had occurred as expected, while XPS studies indicated a stabiliser surface coverage on the PPy particles of around 53 w/v %. PPy particles prepared at lower stabiliser concentrations (20 w/v % based on pyrrole) were not colloidally stable above pH 6. However, higher stabiliser concentrations (50 w/v % based on pyrrole) led to a significant improvement, with colloidal stability being retained above pH 7. Long-term stability studies of PPy particles stored at pH 7.5 confirmed that the amine-based stabiliser produced more stable aqueous dispersions than the imine-based stabiliser, since the latter bond is hydrolytically unstable.

Introduction

Polypyrrole is a relatively air-stable conducting polymer with an electrical conductivity of around 1-10 S cm^{-1} [1-3]. Unfortunately, this material is lightly cross-linked and hence insoluble in all solvents; moreover, it is not melt-processable, so it has very poor processability [4]. In principle, this problem can be alleviated by the preparation of colloidal dispersions of polypyrrole particles via aqueous dispersion polymerisation using chemical oxidants such as $FeCl_3$. This has been readily achieved using commercial water-soluble polymers such as methylcellulose [5], poly(*N*-vinylpyrrolidone) [6], poly(vinyl alcohol) [6-8] or poly(ethylene oxide) [9], which are physically adsorbed at the surface of the polypyrrole particles and hence confer colloidal stability *via* a steric stabilisation mechanism. Such particles are typically around 50 to 300 nm diameter and have a number of potential applications, including synthetic mimics for micrometeorites [10] and intrinsically coloured marker particles for immunodiagnostic assays [11]. Recently it has been shown that poly(vinyl alcohol)-stabilised polypyrrole particles of around 50 nm diameter offer enhanced contrast in the context of optical coherence tomography, which is a medical imaging technique used for the early detection of epithelial cancer [12].

Rather than relying on just physical adsorption, Simmons et al. designed a series of reactive water-soluble steric stabilisers containing either pyrrole or thiophene pendent groups [13,14,15]. This approach leads to *in situ* chemical grafting of the stabiliser chains onto the surface of the growing polypyrrole particles, which in principle should produce polypyrrole particles with better long-term colloidal stability. This route has been shown to be generic, since it allows the rational design of non-ionic, cationic or zwitterionic statistical copolymer stabilisers [13,14,15]. However, one important example has not yet been reported in the literature: primary amine-functionalised sterically-stabilised polypyrrole particles. Primary amines are particularly well suited for aqueous conjugation chemistry, which is attractive for the development of immunodiagnostic assays [11]. In the present work we have designed a new primary amine-based reactive steric stabiliser for the synthesis of primary amine-functionalised polypyrrole particles. Unlike the statistical copolymerisation approach previously reported by Simmons et al. [13,14,15], this new route is based on the chemical modification of a pre-formed primary amine-based water-soluble polymer, poly(vinyl amine) (PVAm). Derivatisation is conveniently achieved using Michael addition to introduce the desired pendent thiophene groups, which has been previously demonstrated to be a pre-requisite for efficient chemical grafting of water-soluble polymer chains onto growing polypyrrole particles. For example, primary amine-functional polymers such as poly(ethylene imine) can be reacted with glutaraldehyde for detection of an antibody (IgG) with enhanced sensitivity and reliability [16]. Chemically modified PVAm has been previously studied by Pelton et al. in the context of its adhesion to cellulose [17,18] but, as far as we are aware, it has not been examined as a steric stabiliser for the synthesis of primary amine-functionalised polypyrrole particles.

Experimental

Materials. Poly(vinyl amine) was donated by BASF (Ludwigshafen, Germany) as a concentrated aqueous solution. 2-Thiophenecarboxaldehyde, $FeCl_3 \cdot 6H_2O$, sodium borohydride, D_2O, NaOH and NaOD were each purchased from Sigma-Aldrich (UK) and were used as received. Methanol and acetone were purchased from Fisher (UK) and used as received. Pyrrole was also purchased from Sigma-Aldrich (UK) and purified by alumina chromatography prior to use. De-ionised water was used in all experiments.

Purification of Poly(vinyl amine). Poly(vinyl amine) (PVAm)

was precipitated from its original aqueous solution (as supplied by the manufacturer) to remove excess salt, which is mainly sodium acetate. Cold acetone (200 ml) was added to PVAm solution (20.0 g) and this mixture was placed in an ice bath for 1 h. Acetone was carefully decanted off and the PVAm precipitate was redissolved in water. Traces of acetone were removed by heating the aqueous solution to 70°C, followed by freeze-drying overnight.

Functionalisation of Poly(vinyl amine) with 2-Thiophenecarboxaldehyde. For all entries shown in Table 1 apart from entry 3, the following protocol was used. PVAm (1.00 g) was dissolved in water (10.0 g) to obtain a 10 w/w % solution. This solution was carefully adjusted to pH 9 using 0.10 M NaOH to avoid precipitation of the PVAm. To target a degree of PVAm derivatisation of 10 mol %, 2-thiophenecarboxaldehyde (0.26 g) was added and the reaction solution was stirred overnight at 60°C. For entry 3 in Table 1, the following slightly modified protocol was used. PVAm (1.00 g) was dissolved in a 9:1 methanol: water mixture (10 ml) to obtain a 10 w/w % solution. 2-Thiophenecarboxaldehyde (0.52 g) was added in order to target a mean degree of derivatisation of 20 mol %. This reaction mixture was placed in an oil bath at 60°C and stirred overnight. For all entries in Table 1, the reaction solution was adjusted to pH 3 using 0.1 M HCl. The derivatised PVAm was purified by washing with ethyl acetate (three 50 ml portions) and the combined aqueous layers were made alkaline (pH 9) by slowly adding 0.10 M NaOH. $NaBH_4$ (0.088 g) was slowly added and the reaction mixture was stirred overnight at 20°C. This derivatised PVAm stabiliser solution was used for the preparation of PPy latexes without further purification. Any background salt present in this solution was removed during purification of the final PPy particles by repeated centrifugation-redispersion cycles.

Preparation of Sterically-stabilised Polypyrrole Particles. First $FeCl_3$ (1.82 g) was dissolved in water (20 ml). Depending on the desired initial stabiliser concentration, the required amount of thiophene-modified (or unmodified) PVAm solution was added to this aqueous oxidant solution, followed by pyrrole (0.20 ml); the resulting polymerising solution was stirred for 16 h to produce a black colloidal dispersion. The polypyrrole particles were purified by centrifugation at 20,000 rpm for 1 h then redispersed in water. This centrifugation-dispersion cycle was repeated a further three times to remove any excess stabiliser, spent oxidant, background salt and any traces of unreacted pyrrole.

Characterisation Techniques.

^1H NMR Spectroscopy. Copolymer stabiliser samples were freeze-dried overnight before being redissolved in D_2O. ^1H NMR spectra were recorded on a 400 MHz Bruker Avance DPX 400 spectrometer.

Transmission Electron Microscopy (TEM). Dilute dispersions (typically < 0.1 w/v %) were dried onto carbon-coated copper grids at ambient temperature and examined using a Philips CM100 electron microscope operating at 100 kV under ultrahigh vacuum conditions.

X-ray Photoelectron Spectroscopy (XPS). The surface compositions of selected polypyrrole particles and appropriate reference materials were examined using a Kratos Axis Ultra DLD x-ray photoelectron spectrometer operating at a base pressure of ~10^{-8} torr. Samples were prepared by drop-casting dilute dispersions onto indium foil. A monochromatic Al X-ray source (10.0 mA, 15 kV) was used. The step size was 1.0 eV for the survey spectra (pass energy = 160 eV) and 0.1 eV for the core-line spectra (pass energy = 20 eV).

Aqueous Electrophoresis. These measurements were conducted in the presence of 1 mM KCl using a Malvern Zetasizer Nano ZS instrument. Zeta potentials were calculated from the electrophoretic mobilities using the Smoluchowski relationship. The solution pH was adjusted from pH 2 to pH 9 by the addition of KOH using a Malvern MPT-2 auto-titrator.

Dynamic Light Scattering (DLS). DLS studies were conducted at 25°C using a Malvern Zetasizer Nano ZS instrument equipped with a 4 mW He-Ne solid-state laser operating at 633 nm. Back-scattered light was detected at 173°, and the mean particle diameter was calculated over thirty runs of 10 seconds duration per run from the quadratic fitting of the correlation function using the Stokes-Einstein equation. All measurements were performed in triplicate on highly dilute aqueous dispersions (typically < 0.01 wt %).

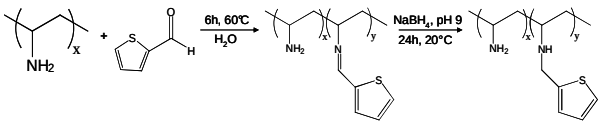

Fig. 1 Reaction scheme for the chemical modification of poly(vinyl amine) via Michael addition using 2-thiophenecarboxaldehyde.

Results and Discussion

Primary amine-based polymers have been examined as reactive steric stabilisers by Li et al. for the aqueous emulsion polymerisation of vinyl monomers such as styrene, *n*-butyl acrylate or methyl methacrylate [19,20]. In this case, the judicious selection of a suitable free radical initiator (e.g. t-butyl peroxide) is essential, since this ensures efficient hydrogen abstraction from the polyamine backbone and hence the generation of reactive polymeric radicals to ensure effective *in situ* grafting to the latex surface. In contrast, we utilise Michael addition in the present work to introduce pendent reactive thiophene groups onto water-soluble poly(vinyl amine) chains; this generic approach is well known to facilitate copolymer stabiliser grafting onto the surface of PPy particles [13,14,15].

In initial experiments, unmodified PVAm was also evaluated as a potential steric stabiliser for PPy particles. This approach was considered at least technically feasible, because it is well known that various water-soluble homopolymers such as poly(*N*-vinyl pyrrolidone) [6] or poly(ethylene oxide) [9] can act as effective steric stabilisers for polypyrrole. However, even when the PVAm precursor was employed at a relatively high initial stabiliser concentration (e.g. 100 % based on the amount of pyrrole monomer), only a macroscopic precipitate of PPy bulk powder was obtained (see entry 1 in Table 1). Thus, unlike some other water-soluble polymers, PVAm is clearly not a suitable polymeric stabiliser for the synthesis of PPy particles.

Table 1. Summary of the extent of thiophene derivatisation of the poly(vinyl amine) precursor, the type of linkage between the poly(vinyl amine) and the pendent thiophene groups, the initial stabiliser concentration (relative to pyrrole monomer) used for the attempted synthesis of colloidal polypyrrole particles, the resulting mean polypyrrole particle diameter and the colloidal stability at pH 7.4 (where applicable).

Entry Number	Thiophene content [a] (mol %)	Imine or Amine linked?	Stabiliser concentration [b] (w/v %)	Particle diameter [c] (nm)	Colloidal stability at pH 7.4 [d]
1	0	n/a	100	ppt	n/a
2	5	Amine	50	ppt	n/a
3	15[e]	Amine	20	115	No
4	10	Amine	10	ppt	n/a
5	10	Amine	20	103	No
6	10	Amine	30	104	No
7	10	Amine	40	95	No
8	10	Amine	50	94	Yes
9	10	Amine	70	89	Yes
10	10	Imine	50	90	Yes

[a] As judged by ^{1}H NMR spectroscopy. [b] Expressed as w/v % relative to pyrrole monomer. [c] Number-average diameter determined by transmission electron microscopy. [d] As judged by visual inspection on standing for 30 minutes at pH 7.4. [e] In this case the Michael addition of PVAm with 2-thiophenecarboxaldehyde was conducted in a 9:1 methanol: water mixture, whereas all other reactions were conducted in pure water.

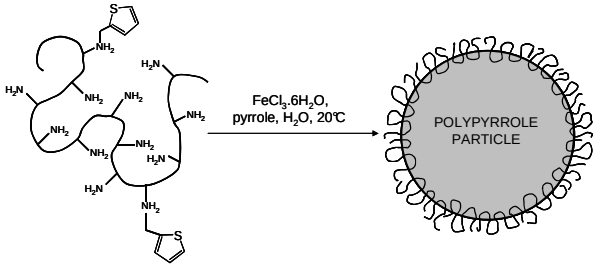

Fig.2 Schematic representation of the formation of sterically-stabilised polypyrrole particles via aqueous dispersion polymerisation at 20 °C using an $FeCl_3$ oxidant and a reactive thiophene-modified poly(vinyl amine) (PVAm) stabiliser.

Figure 1 depicts the synthetic route used to modify PVAm by reacting with 2-thiophenecarboxaldehyde. Each stabiliser was prepared using this protocol, apart from entry number 3 in Table 1. In this case, PVAm was reacted with 2-thiophenecarboxaldehyde in a 9:1 water: methanol mixture, rather than pure water. Originally, it was thought that the methanol co-solvent might be beneficial by adding dissolution of the 2-thiophenecarboxaldehyde reagent. However, it was found that the degree of derivatisation of the PVAm stabiliser was very similar in the presence or absence of methanol, but in the latter case there was no need for an intermediate purification step. In principle, this suggests that a wholly aqueous one-pot route to PVAm-stabilised PPy particles may be feasible. ^{1}H NMR spectroscopy confirmed successful Michael addition between PVAm and 2-thiophenecarboxaldehyde (see Figure 2). The carbonyl group on the 2-thiophenecarboxaldehyde reacts with the primary amine groups on the PVAm chains to form an imine bond. During this reaction, the aromatic NMR signals due to the thiophene-based starting material shift and become much broader as they become grafted to the less mobile polymer chains. The intensity of the carbonyl signal is also reduced, as expected. Spectrum D shows the thiophene-modified PVAm after these imine bonds have been reduced to the corresponding secondary amine bonds using $NaBH_4$. The signal assigned to the two azamethylene protons is more prominent after reduction. The extent of heterocycle incorporation is calculated by comparing the integrated aromatic thiophene signals to those due to the aliphatic PVAm backbone. In the case of one stabiliser, the targeted degree of derivatisation was 20 mol % but subsequent ^{1}H NMR analysis suggested a thiophene content of only approximately 15 mol %. This is because the PVAm chains were partially protonated and hence unable to react with the 2-thiophenecarboxaldehyde via Michael addition. In contrast, when the aqueous solution pH was carefully adjusted to pH 9 using 0.1 M NaOH, the 2-thiophenecarboxaldehyde reaction was highly efficient.

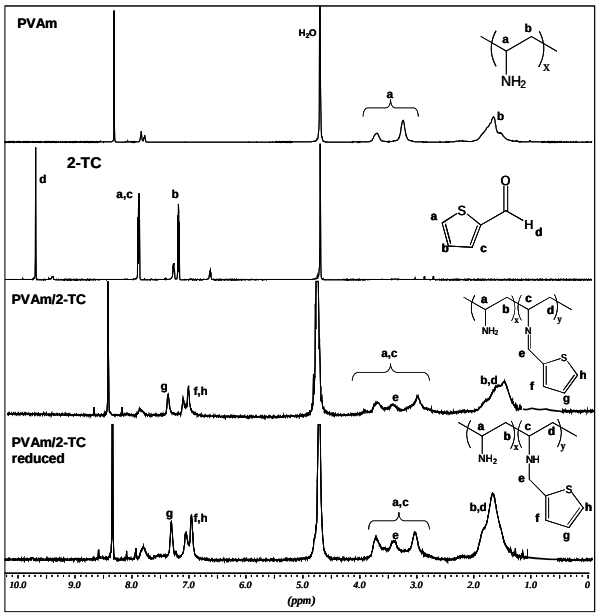

Fig.3 ^{1}H NMR spectra (D_2O) illustrating the chemical modification of poly(vinyl amine) (PVAm) via Michael addition with 10 mol % 2-thiophenecarboxaldehyde, 2-TC: (a) poly(vinyl amine) precursor; (b) 2-thiophenecarboxaldehyde reagent; (c) 2-TC derivatised poly(vinyl amine) with imine linkage (2-TC content = 10 mol %); (d) same 2-TC derivatised poly(vinyl amine) stabiliser after reduction of imine bonds to secondary amine bonds using excess $NaBH_4$.

Figure 3 shows the synthesis of sterically-stabilised polypyrrole particles using the reactive thiophene-functionalised PVAm stabiliser. A minimum thiophene content of at least 10 mol % was required to prevent macroscopic precipitation (compare entry 2 with entries 5-10 in Table 1). Moreover, stable colloidal dispersions are only formed at an initial stabiliser concentration of at least 20 w/v % based on pyrrole. Nevertheless, this stabiliser efficiency is comparable to the various statistical copolymer stabilisers reported by Simmons et al. [13,14,15], which suggests that the thiophene-functionalised PVAm chains act as a relatively efficient reactive stabiliser. Increasing the stabiliser concentration for a given fixed mass of pyrrole monomer produced smaller particle diameters, as expected.

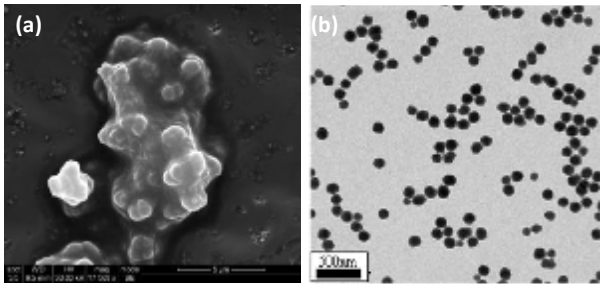

Fig.4 (a) SEM image of PPy bulk powder (b) TEM image of PVAm-stabilised PPy particles (see entry 5 in Table 1).

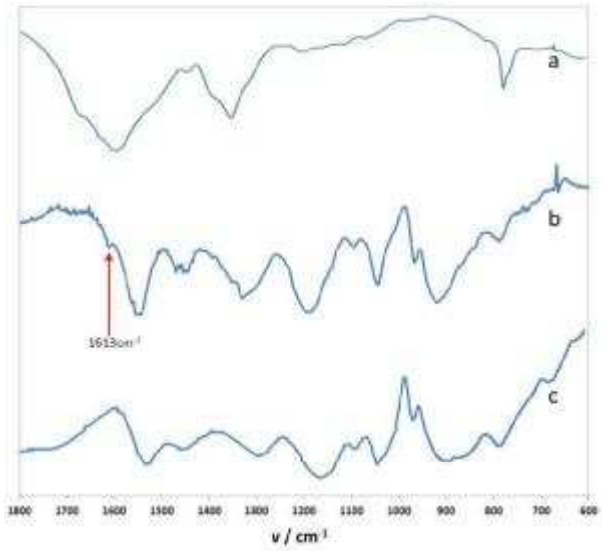

Fig.5 FT-IR spectra recorded for (a) an unmodified PVAm precursor, (b) thiophene-modified PVAm-stabilised PPy particles (see entry 5 in Table 1) and (c) PPy bulk powder. The weak shoulder at around 1613 cm^{-1} confirms that the colloidal PPy particles actually contain the chemically-grafted poly(vinyl amine)-based stabiliser, as expected.

A scanning electron microscopy image of the typical fused globular morphology of PPy bulk powder prepared via precipitation polymerisation in the absence of any polymeric stabiliser is shown in Figure 4a. In contrast, a transmission electron microscopy image of the sterically-stabilised PPy particles prepared using the PVAm-based stabiliser (entry 5 in Table 1) is shown in Figure 4b. The particles have a well-defined spherical morphology and have a relatively narrow size distribution.

FT-IR spectra recorded for the PVAm precursor, PVAm-stabilised PPy particles (see entry 5 in Table 1) and PPy bulk powder are shown together in Figure 5. The PVAm stabiliser has a strong broad band at just above 1600 cm^{-1} which is attributed to the N-H bonds on the chains. This feature is discernible as a weak shoulder at around 1613 cm^{-1} in the spectrum obtained for the PVAm-stabilised PPy particles, which provides useful spectroscopic evidence that the colloidal PPy particles contain significant amounts of PVAm stabiliser. Moreover, the similarity of this latter spectrum to that obtained for PPy bulk powder confirms the doped metallic nature of the PPy chains.

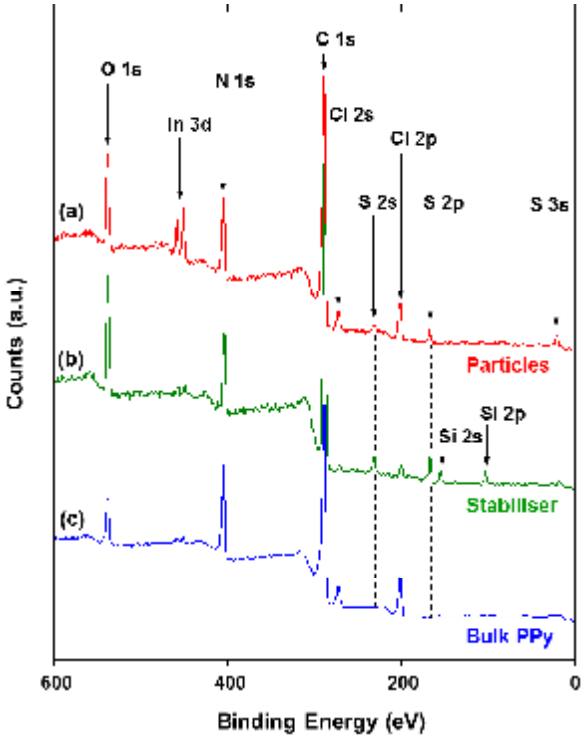

Fig.6 X-ray photoelectron spectra recorded for (a) thiophene-modified PVAm-stabilised PPy particles (entry 5 in Table 1), (b) the corresponding thiophene-modified PVAm stabiliser and (c) a PPy bulk powder reference.

X-ray photoelectron spectra recorded for the PVAm-stabilised PPy particles (entry 5 in Table 1), the corresponding thiophene-modified PVAm stabiliser and also a PPy bulk powder reference are shown together in Figure 6. Here the S2p signal (and also the S2s signal) acts as a unique elemental marker for the thiophene-modified PVAm stabiliser. As indicated by the black dotted lines, these two sulfur signals are present in the spectra recorded for both the thiophene-modified stabiliser and also the PPy particles, but not in that obtained for the PPy bulk powder. Since XPS is highly surface-specific (it has a typical sampling depth of only 2-5 nm), this strongly suggests that the thiophene-modified PVAm stabiliser is located at the surface of the PPy particles, as expected for a chemically-grafted steric stabiliser. Comparing the sulfur surface concentration determined for the PPy particles (~1.1 atom

%) to that in the thiophene-modified PVAm (~3.6 atom %) suggests approximately 53% surface coverage of the PPy particles by the PVAm stabilizer chains. This is perfectly reasonable given that the stabiliser chains are expected to confer only rather patchy surface coverage under ultrahigh vacuum conditions. It is perhaps worth mentioning that, given the chemical grafting mechanism for stabiliser chains, it is conceivable that at least some of the stabiliser is located within the PPy particles, as well as being present at the particle surface.

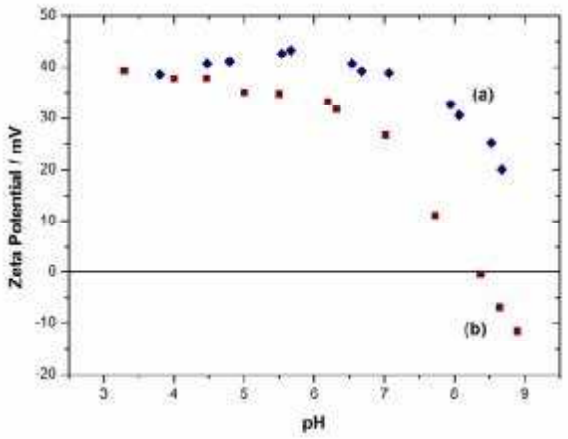

Fig.7 Zeta potential vs. pH curves obtained for PVAm-stabilised PPy particles prepared using: (a) an initial stabiliser concentration of 50 w/v % (relative to pyrrole monomer; see entry 8 in Table 1); (b) an initial stabiliser concentration of 20 w/v % relative to pyrrole monomer; see entry 5 in Table 1).

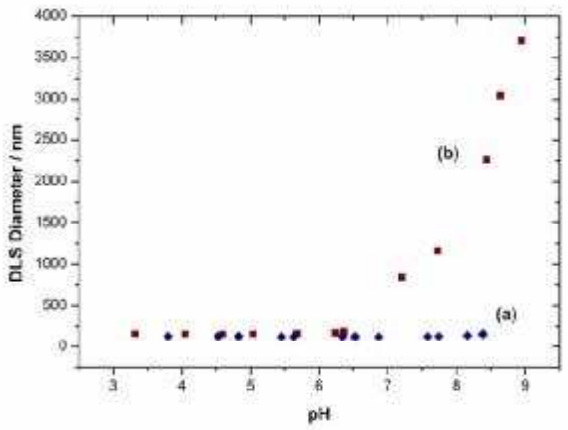

Fig.8 Effect of varying the solution pH on the apparent intensity-average DLS diameter for PVAm-stabilised PPy particles prepared using: (a) an initial stabiliser concentration of 50 w/v % (relative to pyrrole monomer, see entry 8 in Table 1) and (b) an initial stabiliser concentration of 20 w/v % (relative to pyrrole monomer, see entry 5 in Table 1).

Aqueous electrophoresis studies were conducted on PVAm-stabilized PPy particles (see entries 5 and 8 in Table 1) in order to assess their surface charge and also to provide further evidence for the presence of the cationic PVAm stabiliser chains on the PPy particle surface, see Figure 7. Below pH 4, zeta potentials were as high as +40 mV due to protonation of essentially all the primary amine groups on the PVAm chains. This cationic character was reduced at higher pH due to progressive deprotonation of the chemically-grafted stabiliser chains, which have a pK_a of approximately 7.5, as judged by acid titration. Moreover, if a higher initial stabiliser concentration is utilised for these colloid syntheses, this produces PPy particles with greater cationic character. Thus, using 20 w/v % stabiliser based on pyrrole monomer produces PPy particles (entry 5, Table 1) with an isoelectric point of around 8.3, whereas using 50 w/v % stabiliser leads to PPy particles (entry 8, Table 1) that remain substantially cationic at this pH (zeta potential exceeds +25 mV).

The same two colloidal dispersions were also analysed by dynamic light scattering at various solution pH in order to assess their colloidal stability as the PVAm stabiliser chains become deprotonated. In the case of the PPy particles prepared using 20 w/v % stabiliser, the apparent particle diameter increased dramatically from around 180 nm to more than 850 nm above approximately pH 6.3, indicating extensive flocculation under these conditions. Thus this particular colloidal dispersion had very poor stability at physiological pH (pH 7.4), which may be a significant disadvantage if such particles were to be used in immunodiagnostic assays. In contrast, PPy particles synthesised using an initial stabiliser concentration of 50 w/v % proved to be highly stable over the entire pH range studied (up to at least pH 8.4), presumably due to the increased stabiliser coverage of the particle surface in this case. However, increasing the initial stabiliser concentration further to 70 w/v % did not result in any significant improvement in colloidal stability at higher pH (data not shown).

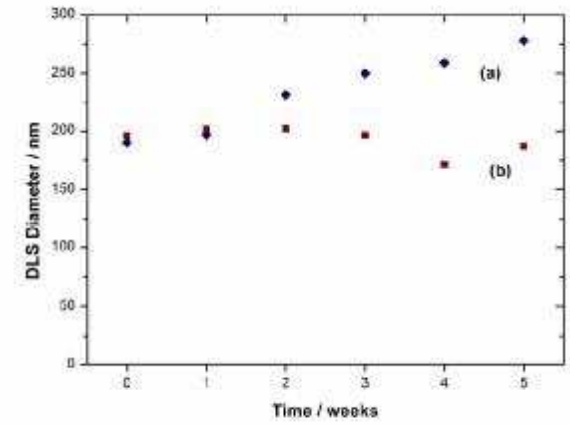

Fig.9 Long-term colloidal stability of PPy particles at pH 7.5 as judged by DLS: (a) prepared at an initial stabiliser concentration of 50 w/v % using imine-linked PVAm (entry 10 in Table 1) and (b) prepared at an initial stabiliser concentration of 50 w/v % using an amine-linked PVAm (entry 8 in Table 1).

The long-term colloidal stability of PVAm-stabilised PPy particles stored at pH 7.5 and 20 ^{o}C was monitored for up to five weeks. Two aqueous dispersions were periodically examined by DLS to assess whether there was any evidence for an increase in the apparent particle diameter. PPy particles synthesised using either an imine-based PVAm stabiliser (entry 10 in Table 1) or an amine-based PVAm stabiliser (entry 8 in Table 1) each had an initial intensity-average diameter of just under 200 nm. However, the apparent size of the former dispersion increased significantly

up to ~280 nm over six weeks, which indicates incipient flocculation, whereas the size of the latter dispersion remained roughly constant. Thus the long-term colloidal stability of PPy particles stored at pH 7.5 is relatively poor if they are prepared using the imine-based stabiliser, presumably due to its slow hydrolytic degradation and de-grafting from the PPy surface. It appears from these preliminary experiments that it is advantageous to use $NaBH_4$ to convert the imine bonds on the stabiliser chains into secondary amine bonds, since the latter are much more hydrolytically stable and hence ensure much better colloidal stability.

Conclusions

Poly(vinyl amine) was successfully derivatised using 2-thiophenecarboxaldehyde to produce a reactive steric stabiliser with pendent thiophene groups. Such stabilisers are readily chemically grafted onto precipitating polypyrrole chains during in situ pyrrole polymerisation to produce sterically-stabilised colloidal particles. These sterically-stabilised particles were spherical, fairly monodisperse and have a mean diameter of around 100 nm as judged by electron microscopy. In contrast, unmodified poly(vinyl amine) is not a suitable polymeric stabiliser for the production of colloidally stable polypyrrole particles, since only a macroscopic precipitate was produced. Various formulations were evaluated for the thiophene-functionalised poly(vinyl amine)-based stabilisers; it was found a thiophene content of less than 20 mol % and an initial stabiliser concentration of less than 20 w/v % (based on pyrrole monomer) invariably resulted in precipitation, rather than a stable colloidal dispersion. Poly(vinyl amine) derivatisation using 2-thiophenecarboxaldehyde was relatively straightforward; in principle, it should be possible to synthesise such a reactive stabiliser, and also the final PPy particles, via a wholly aqueous 'one-pot' synthesis if desired.

XPS studies confirmed unique sulfur signals attributable to the thiophene groups at the surface of the polypyrrole particles. This indicated the presence of the poly(vinyl amine) chains at the particle surface via a chemical grafting mechanism. Aqueous electrophoresis studies suggest that the presence of these poly(vinyl amine) stabiliser chains greatly influence the colloidal stability. The particles are stable at low pH when the pendent amine groups are protonated and the particles are strongly cationic, but this colloidal stability is reduced as the pH is increased. However, using a higher poly(vinyl amine) concentration during the pyrrole polymerisation produces polypyrrole particles that retain their cationic character at higher pH and, perhaps more importantly, lead to improved colloidal stability at physiological pH. Poor long-term colloidal stability was observed at higher pH for the imine-linked poly(vinyl amine) stabiliser; presumably this is due to the well-known hydrolytic instability of imine bonds. This hypothesis is supported by the observation that $NaBH_4$ reduction of these imine bonds to generate more hydrolytically stable secondary amine bonds prior to the synthesis of polypyrrole particles appears to be beneficial. In principle, the primary amine groups on the surface of these polypyrrole particles should allow facile conjugation of bio-markers for immunodiagnostics applications [11, 21-23].

Acknowledgements

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