Synthesis and characterization of sterically stabilized colloidal dispersions of polypyrrole using novel tailor-made water-soluble block copolymers of narrow molecular weight distribution

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Sterically stabilized colloidal dispersions of polypyrrole have been prepared using a novel tailor-made block copolymer stabilizer of narrow molecular weight distribution, synthesized by group-transfer polymerization techniques. These polypyrrole dispersions have a spherical morphology, are slightly flocculated and have a relatively high stabilizer content (54% w/w).

(Keywords: polypyrrole; colloidal dispersions; morphology; synthesis; characterization)

INTRODUCTION

Since 1986 there have been numerous papers describing the preparation of sterically stabilized colloidal dispersions of polypyrrole via dispersion polymerization techniques in both aqueous and non-aqueous media[1-14]. The significance of this approach is that the normally intractable conducting polymer component is obtained in a processable (and hence potentially useful) form. In most cases the steric stabilizers utilized have been commercial polymers such as poly(ethylene oxide)[6,7,10,12], poly(*N*-vinyl pyrrolidone)[2,3,7,10] or poly(vinyl alcohol)[2-4,10]. To the best of our knowledge there is only one report describing the use of a *tailor-made* polymeric stabilizer[15]. However, this poly(2-vinyl pyridine-*co*-n-butyl methacrylate) copolymer was prepared by conventional free-radical copolymerization and consequently possessed a broad molecular weight distribution. Indeed, there are only three literature reports describing the use of 'model' polymeric stabilizers of *narrow* molecular weight distribution to prepare any conducting polymer colloids, and such work has focused exclusively on polyacetylene and polyaniline rather than polypyrrole[16-18]. In the present work we describe for the first time the preparation and characterization of sterically stabilized polypyrrole colloids in aqueous media using a tailor-made block copolymer stabilizer of narrow molecular weight distribution.

EXPERIMENTAL

The poly(*N*,*N*′-dimethylaminoethyl methacrylate-*b*-n-butyl methacrylate) block copolymer was prepared by group-transfer polymerization (GTP)[19,20] at 25°C in a flamed-out reaction vessel using a 1-methoxy-2-methyl-1-trimethylsiloxy propene initiator and a tetrabutylammonium bibenzoate catalyst[21] in tetrahydrofuran (THF) solvent (freshly distilled prior to use) via sequential monomer addition (20 ml *N*,*N*′-dimethylaminoethyl methacrylate polymerized first, followed by 8 ml n-butyl methacrylate). The analogous statistical copolymer was synthesized by pre-mixing the *N*,*N*′-dimethylaminoethyl methacrylate and n-butyl methacrylate comonomers at an initial comonomer molar ratio of 9:1 prior to the GTP copolymerization. Both copolymerizations proceeded rapidly to complete conversion. The resulting copolymers were isolated and dried in a vacuum oven for 16 h overnight.

The polypyrrole colloids were prepared as follows: 0.40 g of the block copolymer and 1.09 g $FeCl_3$ were left to dissolve in 20 ml H_2O for 16 h. Pyrrole (0.20 ml) was then injected into the reaction solution at room temperature with constant stirring. The black solution was stirred for a further 16 h prior to centrifugation at 4000 rev min^{-1} for 2 h. The resulting black sediment was then redispersed in H_2O using an ultrasonic bath. This centrifugation–redispersion cycle was repeated in order to remove excess stabilizer and inorganic salts from the colloid. For certain control experiments (*FT*i.r. and CHN microanalyses) a sample of bulk polypyrrole powder was prepared in the absence of any copolymer stabilizer under the same reaction conditions as the colloid syntheses described above.

RESULTS AND DISCUSSION

The ^1H n.m.r. spectra (250 MHz Bruker AC250SY instrument) and CHN elemental microanalyses (Perkin-Elmer 2400 instrument) of the block and statistical copolymers were self-consistent, and indicated n-butyl methacrylate contents of 29 and 10 mol%, respectively. These copolymer compositions are in good agreement with those expected from our copolymer synthesis conditions. The gel permeation chromatography studies (Perkin-Elmer series 10 liquid chromatograph; THF solvent; Perkin-Elmer LC25 r.i. detector; polystyrene standards) confirmed that both copolymers had unimodal molecular weight distributions. The block copolymer had an M_n of 19 500 and an M_w/M_n of 1.14, whilst the

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statistical copolymer had an M_n of 8300 and an M_w/M_n of 1.10.

The block copolymer stabilizer proved to be an effective, if somewhat inefficient, steric stabilizer for the formation of colloidal polypyrrole particles. On the other hand, use of the statistical copolymer at an identical stabilizer concentration resulted only in a macroscopic precipitate of the conducting polymer. This result is rather surprising in view of the recent characterization of these two copolymer samples by Su and Thomas[22]. In this collaboration both surface tension measurements and neutron reflectivity data on aqueous solutions of the two copolymers suggest that they are almost equally surface active, at least at the air/water interface. Furthermore, the surface tension measurements suggest a critical micelle concentration of less than 0.1 wt% for the block copolymer. This suggests that most (>95%) of the block copolymer molecules are present as multimolecular micelles during the dispersion polymerization of pyrrole, and therefore are not immediately available for adsorption onto the surface of the growing polypyrrole nuclei (such adsorption is a pre-requisite of the steric stabilization mechanism). Thus this may explain why the block copolymer is a relatively inefficient steric stabilizer compared with previously studied steric stabilizers[1-15,23].

The formation of polypyrrole and the presence of the block copolymer stabilizer in the colloidal particles were qualitatively confirmed by *FT*i.r. spectroscopy (Perkin-Elmer 1730 spectrometer) on a colloid film cast onto a CaF_2 disc. This spectrum was consistent with that previously reported for polypyrrole[2], with additional strong absorbances at both 1735 cm^{-1} and 1469 cm^{-1} which are characteristic of the block copolymer stabilizer.

The chemical composition of the polypyrrole colloid was determined from its reduced nitrogen content (9.94%) relative to that of bulk powder polypyrrole prepared under identical conditions in the absence of stabilizer (~15.4%). This method gave a block copolymer stabilizer/polypyrrole mass ratio of 54/46. This value is surprisingly high compared with other polypyrrole–stabilizer systems[4,5,9,14,15], but it is consistent with the observed relative i.r. band intensities due to the polypyrrole and the block copolymer stabilizer in the colloid film spectrum (see above). Recently we have reported similarly high stabilizer contents for poly(ethylene oxide)-stabilized polyaniline dispersions[18].

Thin films fabricated from these colloidal dispersions have conductivities of approximately 1.0 S cm^{-1} as measured by four-point probe techniques, despite the relatively high insulating stabilizer content. These values are comparable to the compressed pellet conductivity of bulk powder polypyrrole[24].

A transmission electron micrograph of a dried down, diluted polypyrrole colloid is shown in *Figure 1*. The polypyrrole particles have a spherical morphology, with an average particle diameter of approximately 50–70 nm. The particles also appear to be somewhat aggregated in the absence of solvent. Photon correlation spectroscopy (Malvern 4700 series PCS system) was used to examine the particle size of the diluted, 'wet' dispersions and preliminary results indicate an intensity-average particle diameter of about 650 nm. Since this value is considerably larger than that observed in the transmission electron microscopy studies, we believe that this particular polypyrrole colloid system, unlike polypyrrole dispersions prepared with other polymeric stabilizers[23], is indeed slightly flocculated in the dispersed state.

Very recently we have reported that the addition of an Fe(II) salt to the pyrrole polymerization reaction solution can reduce the degree of aggregation of the polypyrrole particles[25]. This Fe(II) salt is considered to act as a retarder for the pyrrole polymerization by lowering the oxidation potential of the reaction solution[26].

CONCLUSIONS

It has been shown that a novel tailor-made water soluble block copolymer of narrow molecular weight distribution is an effective steric stabilizer for polypyrrole

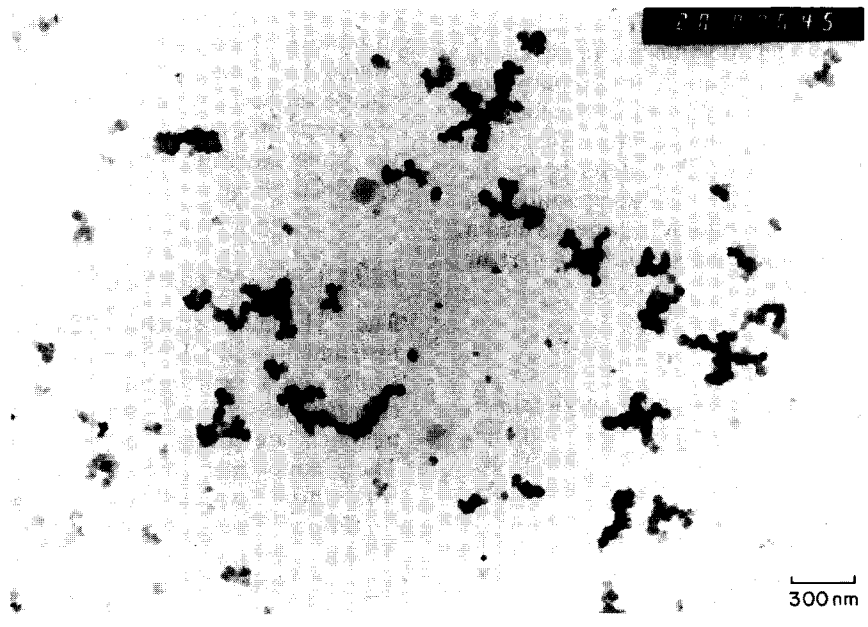

Figure 1 Transmission electron micrograph of a diluted poly(*N,N'*-dimethylaminoethyl methacrylate-*b*-n-butyl methacrylate)-stabilized polypyrrole colloid

colloids. The polypyrrole particles are spherical, slightly flocculated in the dispersed state and have a surprisingly high stabilizer content.

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