Preparation and characterization of colloidal dispersions of polypyrrole using poly(2-vinyl pyridine)-based steric stabilizers

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We describe the preparation of novel colloidal dispersions of polypyrrole in aqueous media via a dispersion polymerization route. Particle aggregation is prevented by a steric stabilization mechanism due to the adsorption of a tailor-made poly(2-vinyl pyridine-co-butyl methacrylate) (P2VP–BM) random copolymer onto the sub-micrometre polypyrrole nuclei. The particle morphology is spherical, as evidenced by transmission electron microscopy, and the average particle diameter could be controlled over the range 130–200 nm by varying the initial P2VP–BM concentration. The adsorbed mass of P2VP–BM per unit mass of polypyrrole was estimated indirectly using Fourier transform infrared spectroscopy. Compressed pellet conductivities of the freeze-dried dispersions were in the range 1–2 S cm^{-1}, despite the presence of the outer layer of adsorbed, insulating stabilizer surrounding each polypyrrole particle. Spin-coating experiments yielded films of similar conductivity and indicate that these polypyrrole dispersions represent a significant improvement in processability over bulk polypyrrole powders. Finally, the base-induced aggregation behaviour of these polypyrrole dispersions was studied with respect to particle concentration and solution pH. Differences between the present system and the poly(4-vinyl pyridine-co-butyl methacrylate)-stabilized polypyrrole dispersion previously investigated are qualitatively explained.

(Keywords: conducting polymer; polypyrrole; poly(2-vinyl pyridine); colloidal dispersions; steric stabilization)

INTRODUCTION

Much of the recent research effort into conducting polymers has been focused on relatively air-stable polyheterocycles such as polythiophene and polypyrrole[1–3]. The poor processability of these materials has been improved by the synthesis of β-substituted derivatives which are soluble in a variety of common solvents[4–10]. However, the β-substituted monomer precursors are often tedious to synthesize, making large-scale production uneconomical. In addition, the solubility of such derivatives is limited, particularly in the doped form.

An alternative approach is the preparation of sterically stabilized conducting polymer colloids via dispersion polymerization. Colloidal forms of three conducting polymers, polyacetylene[11,12], polyaniline[13,14] and polypyrrole[15–20], have been reported to date. The last system has been the most extensively investigated, with various commercial polymers such as poly(vinyl alcohol), poly(vinyl pyrrolidone) and methyl cellulose being shown to be effective in promoting polypyrrole particle formation. Recently, we reported on the use of commercial poly(4-vinyl pyridine)s as steric stabilizers for colloidal polypyrrole[21]. We showed that both poly(4-vinyl pyridine-co-butyl methacrylate) (P4VP–BM) copolymer and high molecular weight poly(4-vinyl pyridine) (P4VP) homopolymer were effective stabilizers. However, lower molecular weight P4VP (≈36 000) and poly(2-vinyl pyridine) (P2VP) were not effective and resulted in macroscopic precipitation of polypyrrole.

In this paper we describe the preparation and characterization of colloidal polypyrrole in aqueous media using a novel tailor-made poly(2-vinyl pyridine-co-butyl methacrylate) (P2VP–BM) random copolymer stabilizer. In addition, we show that P2VP homopolymer can be used as a steric stabilizer for polypyrrole dispersions under certain conditions. Together, these observations provide further insight into the adsorption mechanisms of poly(vinyl pyridine)-based stabilizers onto colloidal polypyrrole particles.

EXPERIMENTAL

Preparation and characterization of steric stabilizers

The P2VP–BM stabilizer was prepared by free-radical copolymerization of 2-vinyl pyridine and butyl methacrylate in toluene at 73°C using 2,2-azobis-isobutyronitrile (AIBN) as an initiator. The copolymer product was purified by repeated precipitation using toluene/n-hexane and methanol/water solvent/non-solvent mixtures before it was finally freeze dried overnight from 1,4 dioxan.

The molecular weights of both the P2VP–BM and the commercially available P2VP homopolymer (Scientific Polymer products) were determined by gel permeation chromatography (American Polymer Standards) using narrow molecular weight P2VP homopolymers as calibration standards. Proton nuclear magnetic resonance (n.m.r.) spectroscopy (JEOL-SX 90 MHz instrument) was used to estimate the relative ratio of the two monomers in the copolymer stabilizer. Elemental microanalyses were determined by Galbraith Laboratories.

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Preparation of (P2VP–BM)-stabilized polypyrrole colloids

The preparation of colloidal polypyrrole has been described in detail elsewhere[15–21]. Briefly, a 1.00 ml aliquot of pyrrole (vacuum distilled from KOH pellets and stored in the dark under argon at −29°C before use) was injected into a 250 ml round-bottom flask containing 100 ml of a stirred, aqueous solution of P2VP–BM and 5.47 g $FeCl_3$ (Aldrich, used as received) oxidant at 25°C. The polymerization was allowed to proceed for at least 24 h; one of us has previously shown that these conditions give a >95% yield of polypyrrole[22]. The excess, non-adsorbed stabilizer and inorganic by-products ($FeCl_2$, HCl, etc.) were then removed by the following procedure. The colloidal particles were spun down at 15 000 rev min^{-1} for 2 h using a J2-21 Beckman centrifuge. The clear yellow–green supernatant was carefully decanted via pipette, and the black sediment was washed several times with 2–3 ml deionized water before it was finally redispersed in water using an ultrasonic bath. A black powder was obtained by freeze drying the concentrated dispersion from water. This synthesis was done at initial steric stabilizer concentrations of 5.0, 7.5 and 10.0 $g\,l^{-1}$.

Characterization of the (P2VP–BM)-stabilized polypyrrole colloids

Particle size and morphology. Transmission electron microscopy studies were made on dilute dispersions dried down on carbon-coated copper grids using a Philips EM 400 instrument. An average particle size was estimated by counting at least 100 particles using a Dapple image analyser.

Visible absorption spectroscopy. A visible absorption spectrum of a diluted, redispersed polypyrrole colloid in water was recorded using a DU-7 Beckman spectrophotometer.

Elemental composition. Microanalyses of powders obtained from (P2VP–BM)-stabilized dispersions were determined by Galbraith Laboratories.

Conductivity. Conductivity measurements were made at 25°C using the standard four-point probe method on compressed pellets of the freeze-dried dispersions. The conductivity of one of these pellets was monitored as a function of time. The conductivity of a thin film of a dispersion cast on a glass slide by a spin-coating process was measured by the same method.

Determination of the adsorbed mass of P2VP–BM stabilizer on the polypyrrole particles. The mass of P2VP–BM stabilizer adsorbed onto the polypyrrole particles was estimated indirectly by analysing the post-reaction supernatants obtained after centrifugation for non-adsorbed P2VP–BM by Fourier transform infrared (*FT*i.r.) spectroscopy. The measurements could not be made on the aqueous supernatants directly due to interference from solvent bands so the following procedure was adopted.

A 1.00 cm^3 (±1%) aliquot of each post-reaction supernatant solution was transferred to a sample vial and placed in a vacuum oven overnight (>15 h) to remove all traces of water. The oven temperature was kept below 80°C to minimize sample degradation. The light green residues were then redissolved in 1.00 cm^3 d_6-DMSO (Aldrich) and stored at room temperature before examination by *FT*i.r. spectroscopy. Six calibration solutions were prepared by dissolving 2–7 mg of P2VP–BM stabilizer in 1.00 cm^3 d_6-DMSO. Each of the nine samples (six calibration solutions and three post-reaction supernatants) were placed in turn in a 100 μm calcium fluoride cell (Spectrotech) and spectra were recorded over the 1100–3000 cm^{-1} middle i.r. region using a Perkin-Elmer FTS-40 spectrometer. The absorbance peaks at 1475 and 1435 cm^{-1} due to the pyridine component of P2VP–BM were used for the quantitative determination of the extent of stabilizer adsorption.

Base-induced flocculation studies. A 2.83×10^{-2} M sodium hydroxide stock solution was titrated against a 3.0 ml (±1%) volume of redispersed (P2VP–BM)-stabilized polypyrrole dispersion at various particle concentrations until flocculation (particle aggregation) was observed. To obtain a suitable concentration, the dispersions were diluted with water, which increased the pH of the dispersion medium. This dilution effect required a correction factor of ≈20% when determining the number of moles of hydroxide ion required to destabilize the dispersions. The end-point pH of each flocculated dispersion was recorded after each titration using a calibrated pH meter.

RESULTS AND DISCUSSION

Gel permeation chromatography (g.p.c.) analysis of the P2VP–BM copolymer indicated an M_n of 42 100 and M_w of 91 700, giving a polydispersity index of 2.18. The commercially available poly(2-vinyl pyridine) homopolymer (nominal manufacturer's molecular weight 200 000) had an M_w of 202 000. The proton n.m.r. spectrum of the P2VP–BM copolymer showed signals in the δ range 6.0–8.6 due to the aromatic protons and 0.0–3.0 due to a combination of aliphatic vinyl and butyl methacrylate protons. The ratio of the two peak integrals indicated that the P2VP–BM copolymer contained ≈5.4 mol% butyl methacrylate. Elemental microanalyses were satisfactory ($\sum[C+H+N+O] > 98.5\%$). The solid state density of P2VP–BM copolymer was estimated to be 1.02 $g\,cm^{-3}$ by weighing a compressed pellet of known dimensions.

Representative transmission electron micrographs for the polypyrrole dispersions prepared at each initial stabilizer concentration are shown together for comparison in *Figure 1*. The average polypyrrole particle diameter, microanalytical data and initial compressed pellet conductivity for each dispersion are presented in *Table 1*.

The visible absorption spectrum of a diluted polypyrrole dispersion was similar to that reported for other polypyrrole colloids, having an absorption maximum at 460 nm and increasing absorption above 600 nm[15,18,21].

Elemental microanalyses of the dry powders obtained from the (P2VP–BM)-stabilized dispersions were different from those reported for bulk polypyrrole powder[22], indicating the presence of the adsorbed P2VP–BM stabilizer. In principle the relative composition of polypyrrole/P2VP–BM in a dispersion could be

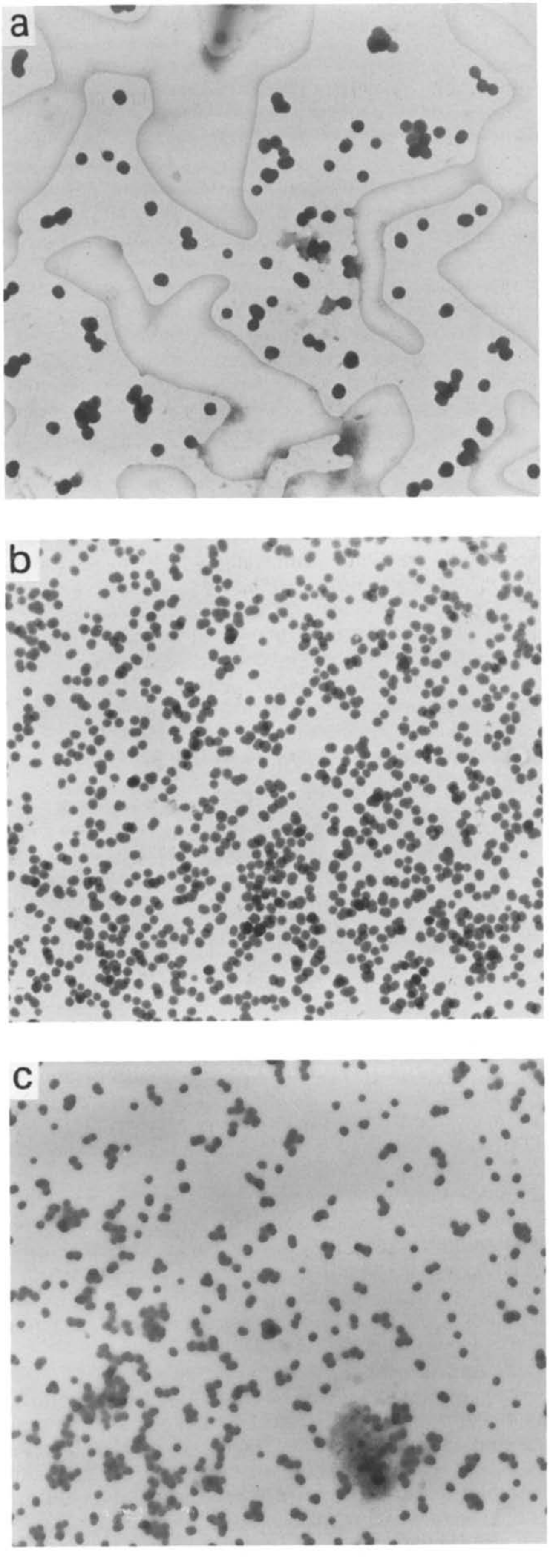

Figure 1 Representative transmission electron micrographs of (P2VP–BM)-stabilized polypyrrole dispersions at three initial stabilizer concentrations (g l^{-1}): (a) 5.0; (b) 7.5; and (c) 10.0

determined from this data but in practice this approach was unreliable. The microanalyses were similar to those previously reported for (P4VP–BM)-stabilized polypyrrole colloids, except that higher concentrations of iron and chlorine were observed in the latter system[21].

Novel dispersions of colloidal polypyrrole can clearly be prepared using a P2VP–BM random copolymer as a steric stabilizer. The average particle diameter decreases with increasing initial stabilizer concentration in a manner similar to that previously reported for other stabilizers such as poly(vinyl alcohol-co-vinyl acetate)[17,18]. This is the first example of the use of a tailor-made stabilizer for the preparation of colloidal polypyrrole.

The decrease in conductivity with time observed for a compressed pellet of a (P2VP–BM)-stabilized polypyrrole dispersion (sample 3, see *Table 1*) exposed to ambient conditions is illustrated in *Figure 2*. For comparison, the decay curves for compressed pellets of bulk polypyrrole powder prepared in the absence of a steric stabilizer using ferric chloride (curve B) and ferric *p*-toluenesulphonate (curve C) are included. (The ferric *p*-toluenesulphonate was prepared by a procedure described by Warren *et al.*[23].) Clearly, the *p*-toluenesulphonate-doped polypyrrole is more air-stable than the chloride-doped material, which in turn is more stable than the chloride-doped, (P2VP–BM)-stabilized dispersion. The poor stability of the composite colloid relative to either of the bulk powders may be due in part to the former's high surface area ($\approx 32\,\mathrm{m^2\,g^{-1}}$): scanning electron microscopy studies of fractured pellets have indicated that the particulate morphology is unchanged by the pelletization process[24]. Ideally, it would be desirable to prepare *p*-toluenesulphonate-doped, (P2VP–BM)-stabilized polypyrrole dispersions using ferric *p*-toluene sulphonate as an oxidant to improve the system's environmental stability. Unfortunately, we found that this oxidant was incompatible with the stabilizer, resulting in the formation of an insoluble yellow–brown complex before pyrrole monomer was added to the reaction solution. However, this approach has been used successfully with other steric stabilizers such as poly(vinyl alcohol-co-vinyl acetate)[24].

All attempts to solution-cast conductive films from aqueous dispersions of the (P2VP–BM)-stabilized dispersions have so far been disappointing. However, our preliminary spin-coating experiments have confirmed that thin films (thickness $\approx 20\,\mu$m) with conductivities comparable to those obtained for the compressed pellets (see *Table 1*) can be easily fabricated.

The mass of P2VP–BM stabilizer adsorbed onto the polypyrrole particles, M_a, was determined using the relationship

$$M_a = M_i - M_s \qquad (1)$$

where M_i is the initial mass of stabilizer dissolved in the reaction solution before the addition of pyrrole monomer, and M_s is the mass of non-adsorbed stabilizer remaining in the post-polymerization supernatant solution (as determined by *FT*i.r. spectroscopy). These calculated values of M_a were used to estimate the adsorbed mass of P2VP–BM stabilizer per unit mass of polypyrrole, assuming the complete conversion of pyrrole monomer to polypyrrole[18,22]. The results (see *Table 1*) indicate that the observed increase in stabilizer adsorption with increasing initial stabilizer concentration

Table 1 Properties of (P2VP–BM)-stabilized polypyrrole dispersions prepared at three different initial stabilizer concentrations

Sample number	Initial stabilizer concentration ($g l^{-1}$)	Average particle diameter (nm)	Compressed pellet conductivity[a] ($S cm^{-1}$)	Microanalytical data C	H	N	O	Cl	Fe	Mass of adsorbed stabilizer[b] (%)	Solid-state adsorbed layer thickness[c] (nm)
1	5.0	203±19	1.6	54.59	4.67	15.62	10.02	14.27	1.06	10.4	5±2
2	7.5	155±19	1.2	55.57	4.49	15.19	9.15	14.45	1.15	11.8	4±1
3	10.0	134±15	2.2	54.42	4.41	14.94	8.95	15.09	1.26	16.7	6±2

[a] Initial value for a fresh pellet

[b] As determined by *FT*i.r. spectroscopy (assuming 100% conversion of pyrrole to polypyrrole)

[c] Calculated by assuming a uniform distribution of adsorbed stabilizer around each polypyrrole particle

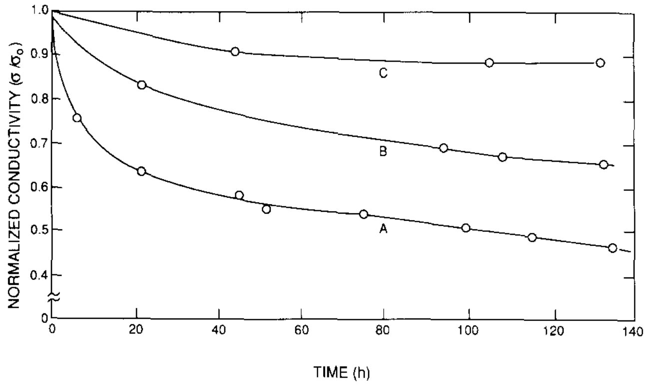

Figure 2 Conductivity decay curves for compressed pellets of: A (P2VP–BM)-stabilized polypyrrole dispersion; B bulk polypyrrole prepared with ferric chloride; C bulk polypyrrole prepared with ferric *p*-toluenesulphonate

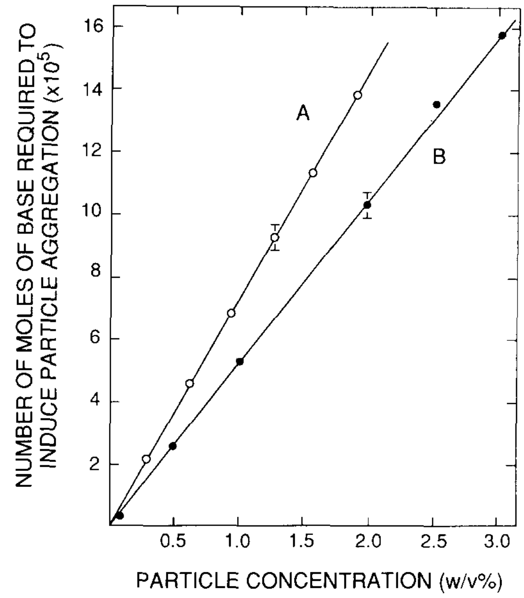

Figure 3 Number of moles of base required to induce particle aggregation as a function of particle concentration: A (P2VP–BM)-stabilized polypyrrole dispersion (end-point pH 5.2±0.1); B (P4VP–BM)-stabilized polypyrrole dispersion (end-point pH 3.6±0.1)

arises from the concomitant increase in total surface area of the dispersion due to the reduced particle size. Indeed, we find that the mass of adsorbed stabilizer is proportional to the total surface area of the polypyrrole particles, at least within experimental error.

Based on the above results, and assuming that a uniform layer of stabilizer surrounds each polypyrrole particle in the solid state, we may estimate the thickness (δ) of this stabilizer layer (see *Table 1*). However, the relatively high compressed pellet conductivities (1.2–2.2 S cm^{-1}) suggest that the polypyrrole particles are nearer to each other and we therefore conclude that the stabilizer layer is of non-uniform thickness in the solid state.

The number of moles of base (hydroxide ion) required to induce particle aggregation in a (P2VP–BM)-stabilized dispersion (sample 2) over a particle concentration range of 0.3–1.9 wt% is depicted in *Figure 3*. Our previously reported data for (P4VP–BM)-stabilized polypyrrole dispersions is included for comparison[21]. A qualitative explanation of the microscopic processes that occur during the base-induced flocculation of the latter system has already been proposed and is equally applicable to the (P2VP–BM)-stabilized dispersion[21]. However, it is evident from *Figure 3* that the aggregation phenomena observed for these two systems differ in some quantitative aspects. This is not unexpected since the colloidal stability of sterically stabilized dispersions is generally determined by the nature of the outer layer of adsorbed stabilizer. Thus we find that, for any given solids concentration, the (P2VP–BM)-stabilized dispersions require more basic conditions (pH = 5.2±0.1) before flocculation is observed than the (P4VP–BM)-stabilized dispersions (pH = 3.6±0.1). We conclude that the pyridine rings of the adsorbed P2VP–BM stabilizer are more easily protonated (and, therefore, more solvated in less acidic media) than those of the P4VP–BM stabilizer. Other workers have reached similar conclusions in investigating the solution behaviour of poly(2- and 4-vinyl pyridine) homopolymers in acidic media[25].

Since particle aggregation in either system occurs under relatively acidic conditions it is possible to avoid deprotonation of the polypyrrole component of the colloid (which would otherwise result in a concomitant loss in conductivity[26]) and thereby produce conducting particle aggregates. This may prove useful for certain commercial applications.

Previously we have reported that poly(2-vinyl pyridine) homopolymer does not produce stable polypyrrole dispersions even at initial stabilizer concentrations as high as 12.0 $g l^{-1}$. It was believed that the hydrogen bond interaction between the pyridine ring nitrogen and the polypyrrole surface (see *Figure 4a*) was too weak to promote sufficiently strong and/or complete adsorption of the stabilizer, which is a necessary prerequisite for effective steric stabilization. In contrast, we have shown that the analogous poly(4-vinyl pyridine) homopolymer produces stable polypyrrole dispersions

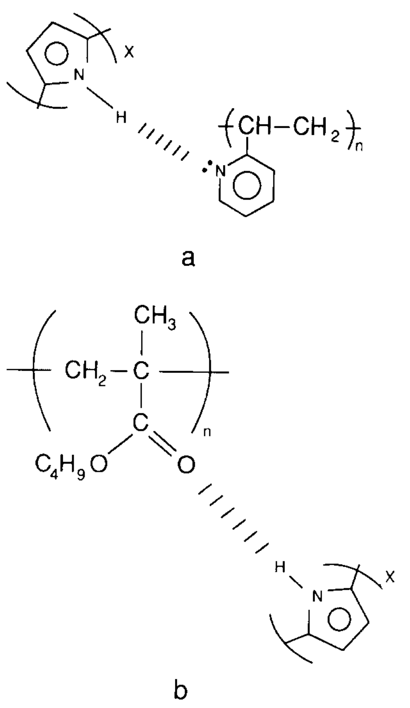

Figure 4 Probable adsorption modes of steric stabilizers on polypyrrole particles: (a) P2VP homopolymer; (b) P2VP–BM copolymer

under identical conditions[21]. Thus, we must attribute the efficient adsorption of the P2VP–BM copolymer at initial stabilizer concentrations as low as $5.0\,\mathrm{g\,l^{-1}}$ to the hydrophobic butyl methacrylate component (see *Figure 4b*). There are two possible reasons for the poor adsorption of the P2VP homopolymer: (1) steric hindrance from the hydrocarbon polymer backbone precludes the hydrogen bonding interaction; (2) too many pyridine ring nitrogens are protonated (and therefore are incapable of interacting with the pyrrole N–H moiety) under the highly acidic reaction conditions of the pyrrole polymerization. We reiterate that previous workers have shown that P2VP is more fully protonated than P4VP at any given pH[25].

We attempted to distinguish between these two possibilities by devising a control experiment. A Lewis base (pyridine) was added to the reaction solution to reduce the solution acidity and thereby lower the degree of protonation of the P2VP homopolymer. This would produce more pyridine nitrogen lone-pairs per stabilizer molecule capable of adsorption via the hydrogen bond interaction illustrated in *Figure 4a*. Briefly, 1.0 ml pyridine was added to a stirred aqueous solution containing 5.47 g $FeCl_3$ oxidant and P2VP homopolymer (initial stabilizer concentration $12.0\,\mathrm{g\,l^{-1}}$) before the addition of pyrrole monomer. As already stated, the stabilizer does not normally prevent macroscopic precipitation. However, in the presence of pyridine, a colloidal dispersion of polypyrrole particles is obtained[27]. Thus we conclude that the non-adsorption of the P2VP homopolymer in the absence of pyridine is primarily due to the high degree of protonation of the pyridine ring nitrogens rather than because of any significant steric hindrance effects.

CONCLUSION

A novel tailor-made P2VP–BM random copolymer has been shown to be an effective steric stabilizer for polypyrrole colloids. We believe that stabilizer adsorption is primarily due to the hydrophobic butyl methacrylate component, probably via a hydrogen-bonding mechanism with the pyrrole N–H group. The particle size of the dispersion decreases with increasing stabilizer concentration and could be varied over the range 130–200 nm. The adsorbed mass of stabilizer per unit mass of polypyrrole was estimated indirectly by *FT*i.r. spectroscopy. Simple calculations based on these measurements indicate a solid state adsorbed stabilizer layer thickness of ≈5 nm, which seems high in view of the initial compressed pellet conductivities ($1–2\,\mathrm{S\,cm^{-1}}$). Spin-coating methods can also be used to fabricate thin films of comparable conductivity from aqueous dispersions of these polypyrrole colloids.

Preliminary studies indicate that this colloidal form of polypyrrole is less environmentally stable with respect to conductivity than bulk polypyrrole powder, possibly due to the former's relatively high surface area ($\approx 32\,\mathrm{m^2\,g^{-1}}$).

These (P2VP–BM)-stabilized polypyrrole dispersions require more base to induce particle aggregation than (P4VP–BM)-stabilized dispersions for a given particle concentration. Aggregation occurs at a solution pH of 5.2 ± 0.1 regardless of the particle concentration. Deprotonation of the pyrrole N–H moiety does not occur under these conditions, and thus the aggregated particles retain their high electrical conductivity.

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REFERENCES

1 Skotheim, T. A. (Ed.) 'Handbook of Conducting Polymers', Dekker, New York, 1985
2 'Proceedings of the International Conference on the Science and Technology of Synthetic Metals' (ICSM '86) *Synth. Met.* 1987, 17–19
3 'Proceedings of the International Conference on the Science and Technology of Synthetic Metals' (ICSM '88) *Synth. Met.* 1989, **28**(1–2)
4 Jen, K.-Y., Miller, G. G. and Elsenbaumer, R. L. *J. Chem. Soc. Chem. Commun.* 1986, 1346
5 Havinga, E. E., van Morssen, L. W., ten Moeve, W., Wynberg, H. and Meijer, E. W. *Polym. Bull.* 1987, **18**, 277
6 Patil, A. O., Ikenoue, Y., Wudl, F. and Heeger, A. J. *J. Am. Chem. Soc.* 1987, **109**, 1858
7 Yoshino, K., Nakajima, S. and Sugimoto, R. *Jpn J. Appl. Phys.* 1987, **26**(6), 1038
8 Roncali, J., Garreau, R., Yassar, A., Marque, P., Garnier, F. and Lemaire, M. *J. Phys. Chem.* 1987, **91**, 6706
9 Ezquerra, T. A., Ruhe, J. and Wegner, G. *Chem. Phys. Lett.* 1988, **144**, 194
10 Bryce, M. R., Chissel, A., Kathirgamanthan, P., Parker, D. and Smith, N. R. M. *J. Chem. Soc. Chem. Commun.* 1987, 466
11 Edwards, J., Fisher, R. and Vincent, B. *Makromol. Chem. Rapid Commun.* 1983, **4**, 393
12 Armes, S. P. and Vincent, B. *Synth. Met.* 1988, **25**, 171
13 Cooper, E. C. *PhD Thesis* University of Bristol, UK, 1988
14 Armes, S. P. and Aldissi, M. *J. Chem. Soc. Chem. Commun.* 1989, 88
15 Bjorklund, R. B. and Liedberg, B. *J. Chem. Soc. Chem. Commun.* 1986, 1293
16 Armes, S. P. and Vincent, B. *J. Chem. Soc. Chem. Commun.* 1987, 288

17 Armes, S. P., Miller, J. F. and Vincent, B. *J. Colloid. Interface Sci.* 1987, **118**, 410
18 Armes, S. P. *PhD Thesis* University of Bristol, UK, 1987
19 Cawdery, N., Obey, T. M. and Vincent, B. *J. Chem. Soc. Chem. Commun.* 1988, 1189
20 Armes, S. P. and Aldissi, M. *Synth. Met.*, in press
21 Armes, S. P., Aldissi, M. and Agnew, S. F. *Synth. Met.* 1989, **28**, C837
22 Armes, S. P. *Synth. Met.* 1987, **20**, 367
23 Walker, J. A., Warren, L. F. and Witucki, E. F. *Am. Chem. Soc. Polym. Prepr.* 1987, **28**(2), 256
24 Armes, S. P. unpublished results
25 Molyneux, P. 'Water-soluble synthetic polymers: properties and behaviour', Vol. II, CRC Press, Florida, 1983 and references therein
26 Munstedt, H. *Polymer* 1986, **27**, 899
27 Armes, S. P. and Aldissi, M. Patent pending, DOE Case Number S66,842