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TITLE: Poly(Vinyl Pyridine)-Based Stabilizers for Aqueous Polypyrrole Latices

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POLY(VINYL PYRIDINE)-BASED STABILIZERS FOR AQUEOUS POLYPYRROLE LATICES

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ABSTRACT

The preparation and characterization of sub-micronic polypyrrole latex particles using polymeric stabilizers based on poly(vinyl pyridine) is described. These novel colloidal dispersions enhance the usually limited processability of the electroactive component, and in addition exhibit usefully high solid-state conductivity (∿2 Scm^{-1}), despite the presence of the insulating stabilizer component. Furthermore, these latices exhibit reversible base/acid induced flocculation-stabilization behavior. The latter phenomenon is of fundamental interest and is expected to have commercial applications.

The latices were characterized by transmission electron microscopy, visible absorption spectroscopy, F.T.I.R. and Raman spectroscopy, microanalysis, and compressed pellet d.c. conductivity. Base-induced particle flocculation was studied as a function of latex particle concentration.

INTRODUCTION

Since 1979, polypyrrole has been recognized as a relatively air-stable conducting polymer [1-3]. Recently, several groups have described the preparation of sub-micronic polypyrrole latex particles [4-11]. Some of these systems are thermodynamically stable with respect to flocculation (particle aggregation) and offer significant advantages in processability relative to the insoluble bulk powders or films obtained by standard chemical synthesis techniques [12-14]. Macroscopic precipitation is prevented by a thin, physically-adsorbed outer layer of a suitable macromolecular surfactant (the so-called "steric stabilization" mechanism [15,16]). Several commercially available polymers, such as poly(vinyl alcohol-co-acetate) [PVA], poly(vinyl pyrrolidone) [PVP], poly(acrylamide) [PAA], methylcellulose [MC], and poly-(ethylene oxide) [PEO] have been reported to be successful in acting as steric stabilizers and promoting discrete particle formation. Surprisingly, the presence of these insulating, adsorbed macromolecules does not seem to significantly reduce the solid-state conductivity of either films or pellets fabricated from these polypyrrole latices relative to that of bulk polypyrrole. Various values between 0·2 and 5·0 Scm^{-1} have been reported for such systems [4-9].

In this publication we report the preparation and characterization of similar polypyrrole latices synthesized using novel steric stabilizers based on poly(4-vinylpyridine). The use of such stabilizers allows unique control over the colloidal stability of the latices, which may prove to be useful in the large-scale preparations necessary for commercial applications of these processable form of polypyrrole.

EXPERIMENTAL

Pyrrole (Aldrich) was vacuum-distilled from KOH pellets and stored under argon at -29°C prior to use. Anhydrous $FeCl_3$ (E. M. Sciences) was used as received. De-ionized water was used in all reactions.

Poly(4-vinyl pyridine) [P4VP(I); nominal M.W. ∿50,000] was purchased from Polysciences. Poly(4-vinyl pyridine) [P4VP(II); nominal M.W. ∿200,000] and poly(4-vinyl pyridine-co-butyl methacrylate) [P4VP-BM; nominal M.W. $\sim 10^5$] were supplied by Scientific Polymer Products. All four samples were used as received.

(i) Characterization of the commercial polymeric stabilizers:

Gel permeation chromatography (G.P.C.) calibrated with narrow molecular weight poly(2-vinyl pyridine) standards [American Polymer Standards Company] was used to characterize the commercial P2VP sample (see Table 1). Poly(4-vinyl pyridine) is not amenable to G.P.C. analysis [17] so the two homopolymer samples P4VP(I) and P4VP(II) were analyzed by differential viscometry in ethanol (Viscotek Corp.). The molecular weights were determined using the literature values for the Mark-Houwink constants K and a given by Fuoss _et. al._ [18] (See Table 1). The poly(4-vinylpyridine-co-butyl methacrylate) copolymer was not soluble in ethanol so differential viscometry measurements were made in methanol using the two commercial poly(4-vinyl pyridine) samples as calibration standards to obtain an estimate of the molecular weight. The 4-vinylpyridine/butyl methacrylate monomer mole ratio in the copolymer was determined to be ∿15·4:1 using ^1H n.m.r. spectroscopy (JEOL-SX 900 instrument; deuterochloroform solvent).

(ii) Latex synthesis:

The polypyrrole latices were prepared via an aqueous dispersion polymerization route similar to that previously described [6-8]. Briefly, 1·0 ml of pyrrole was injected into a 250 ml round-bottom flask containing 100 ml of a stirred, aqueous solution of the steric stabilizer and $FeCl_3$ oxidant at room temperature and was stirred for at least 24 h at room temperature, conditions which one of us has previously shown leads to >95% yield of polypyrrole [19]. In the event of ineffective steric stabilization, macroscopic precipitation of polypyrrole was observed within a few minutes and no further characterization was attempted. After 24h the excess, non-adsorbed stabilizer, and inorganic by-products were removed by spinning down the latex particles at ∿15,000 r.p.m. for 1-3h using a J2-21 Beckman model centrifuge. The clear yellow-green supernatant was carefully decanted via pipette, and the black sediment was washed several times with 2-3 ml of water before finally redispersed in water using an ultrasonic bath. Latex powder was obtained by freeze-drying from water. Each of the four commercial polymers were used at various concentrations in attempts to prepare sterically-stabilized polypyrrole latex.

(iii) Latex characterization:

In the present work we will focus on the characterization of the polypyrrole latices produced using the P4VP-BM copolymer.

(a) Particle size and morphology: transmission electron microscopy studies were made on diluted, redispersed latex dried down on carbon-coated copper grids using a Philips EM410 instrument. An average particle size was estimated by counting >100 particles. A compressed pellet of the latex powder was fractured for inspection by scanning electron microscopy. This sample was gold-coated and examined using a CAMSCAN series 4 instrument.

(b) Conductivity: measurements were made using the standard four-point probe method on compressed pellets of the freeze-dried latex powder. The conductivity of several pellets were monitored as a function of time.

(c) Spectroscopy: A visible absorption spectrum of diluted, redispersed polypyrrole latex in water was recorded using a DU-7 Beckman visible absorption spectrophotometer. An F.T.I.R. spectrum of the freeze-dried latex powder dispersed in a KBr disc was recorded using a Biorad Digilab FTS-40 instrument.

(d) Elemental composition: microanalysis of various (P4VP-BM)-stabilized polypyrrole latices were determined by Galbraith labs.

(e) Adsorbed amount of steric stabilizer: The amount of P4VP-BM stabilizer adsorbed onto the polypyrrole particles was determined indirectly by analyzing the clear yellow-green post-reaction supernatants obtained after centrifugation for non-adsorbed P4VP-BM by Raman spectroscopy. A 130°C back-scattering experimental set-up was employed, utilizing an argon ion laser

(λ = 457·9 nm; power ~250mW; slit resolution 5 cm^{-1}; spectral band width 5 cm^{-1}). The concentration dependence of the intensity of the 1009 cm^{-1} peak due to the pyridine ring C-H symmetry deformation made was obtained using P4VP-BM calibration standards of known concentration in dilute HCl. The solvent peak at 3420 cm^{-1} was used as an internal standard to normalize the 1009 cm^{-1} peak intensities. By measuring the 1009 cm^{-1} peak intensity in the supernatant solutions and using the calibration curve the supernatant stabilizer concentration was determined. Hence, the adsorbed amount of P4VP-BM stabilizer was calculated from the difference between the known initial stabilizer concentration and the measured final stabilizer concentration.

(f) Flocculation experiments: a 5·55 x 10^{-2}M NaOH stock solution was titrated against a 3·0 ml volume of redispersed, (P4VP-BM)-stabilized polypyrrole latex of various concentrations until particle aggregation was observed. In order to obtain a suitable concentration range the dispersions were diluted with water, which increased the pH of the dispersion medium. This effect required a correction factor of ~30% when determining the number of moles of hydroxide ion required to destabilize the dispersions.

RESULTS

The P2VP and P4VP(I) homopolymers were ineffective steric stabilizers and did not prevent macroscopic polypyrrole precipitation (see Table 1).

Table 1: Effect of using various commercial poly(vinyl pyridine)s as steric stabilizers for polypyrrole latex.

Sample	Molecular Weight (g/mol)	Stabilizer Concentration (g/l)	Latex Formation (x/✓)	Average Particle Diameter (nm)
P2VP	202,000[a]	12.0	x	—
P4VP (I)	38,000[b]	12.0	x	—
P4VP (II)	218,000[b]	12.0[c]	✓	150
P4VP-BM	~405,000[b]	4.5	✓	85

a. Weight - Average Molecular Weight.

b. Viscosity - Average Molecular Weight.

c. Some Macroscopic Precipitation of Polypyrrole Observed.

In contradistinction, both the P4VP(II) homopolymer and the P4VP-BM copolymer promoted the formation of stable, aqueous dispersions of polypyrrole particles. With the former stabilizer some precipitation was observed even at initial concentrations as high as 12·0 g/l. However, the P4VP-BM copolymer was markedly more efficient with negligible precipitation being observed at stabilizer concentrations as low as 4·5 g/l. Figure 1 depicts a typical transmission electron micrograph of a (P4VP-BM)-stabilized polypyrrole latex.

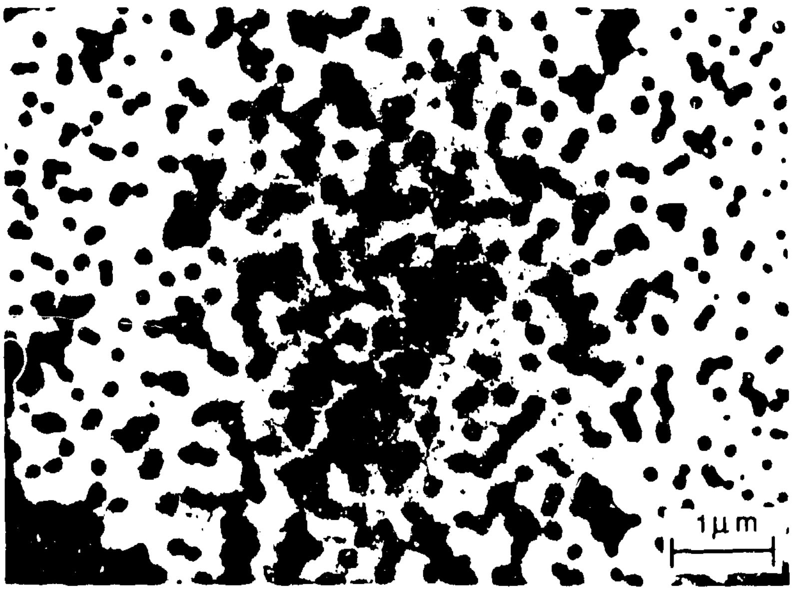


Figure 1: Transmission electron micrograph of a (P4VP-BM)-stabilized polypyrrole latex. Initial stabilizer concentration = 4·5 g/l.

The average latex particle diameter, pellet d.c. conductivity, microanalysis and amount of adsorbed stabilizer for various initial P4VP-BM stabilizer concentrations are given in Table 2. The conductivity of several latex pellets exposed to the ambient atmosphere decreased by 40-60% within 20-30h. No long-term studies have been undertaken at the present time.

Both the visible absorption and F.T.I.R. spectra were very similar to those reported previously for MC- and PVA-stabilized polypyrrole latices [4,8]. In the latter case, no absorption bands attributable to the P4VP-BM stabilizer were observed.

Scanning electron microscopy (S.E.M.) Of the fractured pellet clearly revealed that the latex particles had retained their original size and shape, and were essentially unchanged by the pelletization process.

The results of the Raman measurements on the post-reaction supernatant solutions produced a linear calibration curve. Using this curve the approximate mass of adsorbed P4VP-BM stabilizer was calculated for various initial stabilizer concentrations (see Table 2).

Table 2: Characterization of (P4VP-BM)-stabilized polypyrrole latices prepared at various initial stabilizer concentrations.

Sample Number	Stabilizer Concentration (g/l)	Average Particle Diameter (nm)	Mass of Adsorbed Stabilizer (gms)	Microanalysis Data (%)						Conductivity (S cm^{-1})
				C	H	N	O	Cl	Fe	
1‡	4.0	92 ± 11	0.23 ± 0.03	50.20	4.02	13.38	7.74	20.89	3.71	2.0
2	4.5	85 ± 13	0.32 ± 0.08	50.02	3.59	13.18	7.95	21.02	4.50	0.9
3	5.0	112 ± 15	0.28 ± 0.04	49.18	4.03	12.96	7.27	20.38	5.52	2.1
4	6.0	88 ± 14	0.33 ± 0.02	48.17	4.13	12.52	9.93	19.36	5.47	0.4

‡ Some Macroscopic Precipitation of Polypyrrole Observed.

The relationship between latex concentration and the number of moles of hydroxide ion required to induce flocculation is shown in Figure 2. The error bars are an indication of the uncertainty in the visual determination of the flocculation end-point. The flocculated dispersions had a pH of 3·6 ± 0·1 regardless of initial latex concentration.

DISCUSSION

It has been shown that two poly(4-vinyl pyridine)-based stabilizers can be used to prepare colloidal dispersions of polypyrrole. This extends the number of known dispersants to seven, the others being PVA, PVP, PAA, MC, and PEO. It is believed that, in the case of the P4VP-BM copolymer, the hydrophobic butyl methacrylate component is bound to the polypyrrole particle core <u>via</u> a hydrogen-bonding type interaction (see Figure 3a). This adsorption mechanism has been previously postulated by one of us for the PVA and PVP stabilizers [8]. However, this explanation is precluded for the P4VP(II) homopolymer due to the absence of C=O moieties, thus we propose an analogous hydrogen

Figure 2: Number of moles of hydroxide ion required to induce particle flocculation in 3·0 ml of latex as a function of latex concentration.

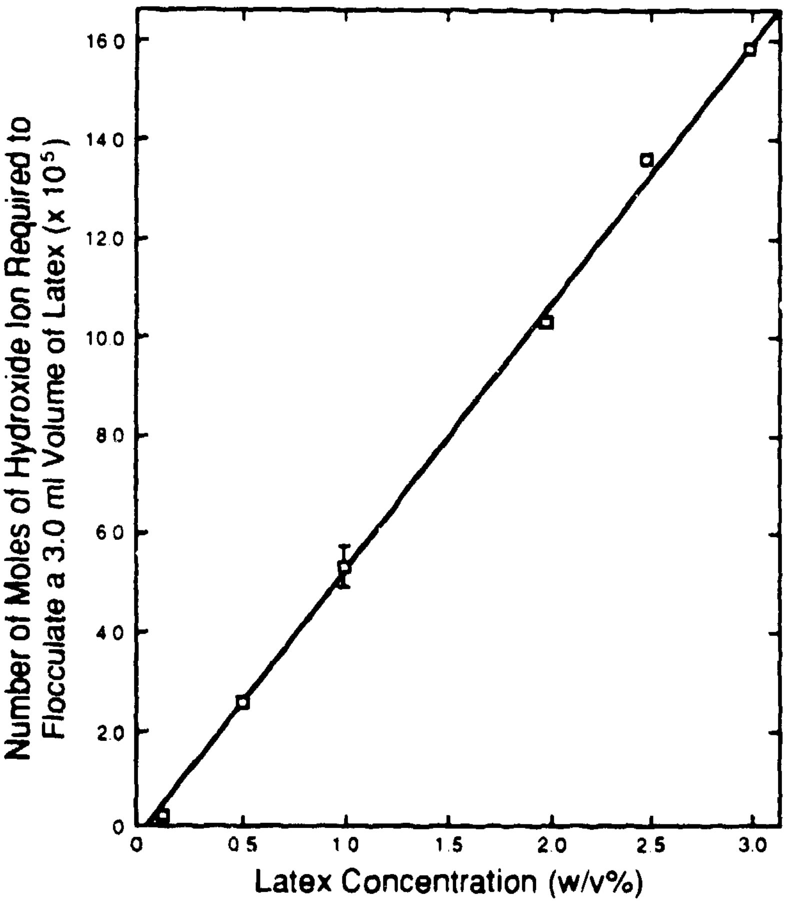
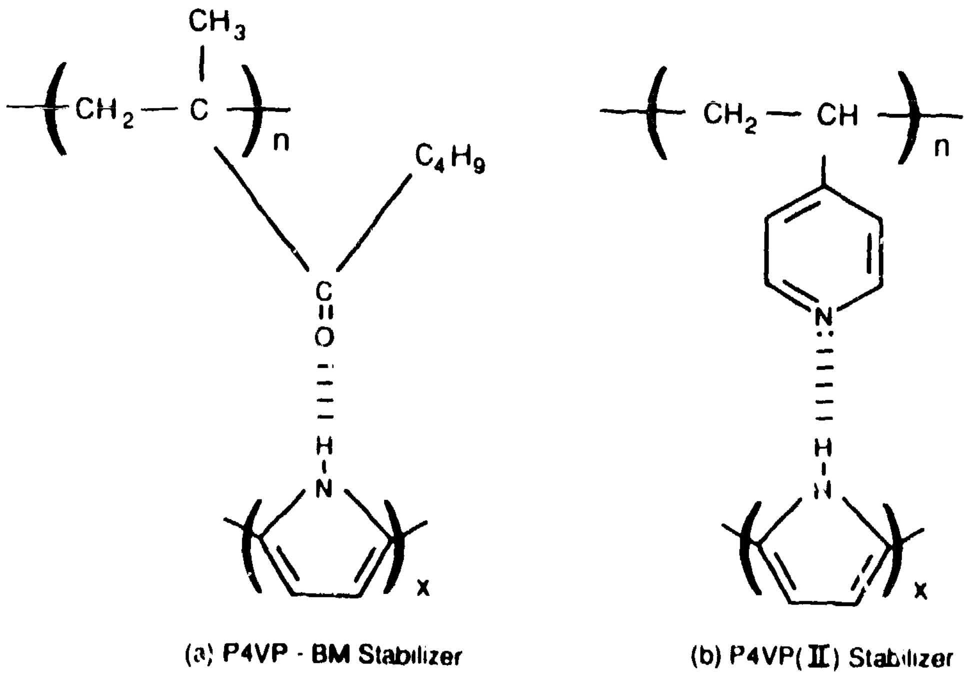


Figure 3: Probable adsorption mechanisms for (a) P4VP-BM and (b) P4VP(II) stabilizers onto polypyrrole latex.

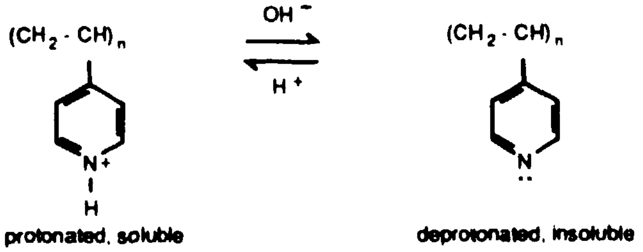


bonding interaction via the lone-pair of the pyridine nitrogen (Figure 3b). X-ray crystallographic data obtained from protein studies [20] suggest the latter interaction to be weaker, which may explain the observed decreased stabilizer efficiency of the P4VP(II) homopolymer relative to the P4VP-BM copolymer. It is of interest to note that the observed molecular weight dependence of the P4VP homopolymer stabilizer efficiency is similar to that reported for PVP homopolymer [8]. Thus, P4VP (M.W. 36,000) and PVP (M.W. 44,000) do not prevent macroscopic polypyrrole precipitation, whereas P4VP (M.W. 217,000) and PVP (M.W. 360,000) are effective dispersants at the same respective stabilizer concentrations.

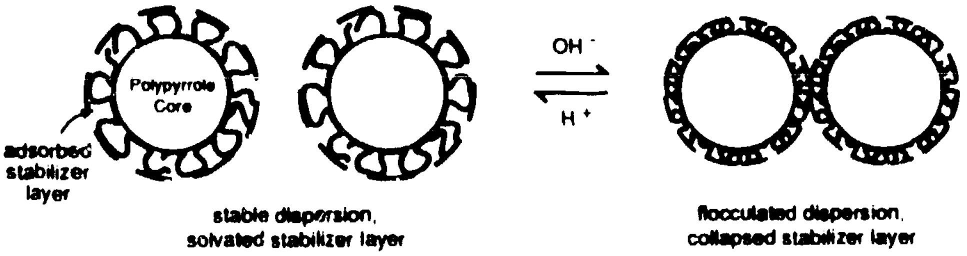
It is known that the 2- and 4-isomers of poly(vinyl pyridine) are insoluble in water [21]. However, they behave as polyelectrolytes in acid media, dissolving readily due to protonation of the weakly basic pyridine group at the ring nitrogen (see Figure 4a).

Figure 4: Schematic representation of the base/acid induced flocculation/destabilization on an (a) microscopic scale, (b) macroscopic scale.

(a) Microscopic Picture:



(b) Macroscopic Picture:



In the described synthesis of polypyrrole colloids, the reaction solution has an initial pH <2·0 and a post-reaction pH <0·0 (the extra activity is due to the loss of the α-pyrrole protons). In view of the acid-induced ionization of the P4VP and P4VP-BM stabilizers, we cannot rule out an electrostatic contribution to the usual steric stabilization mechanism. Indeed, we have observed that these polyelectrolyte-stabilized polypyrrole latices can be salted-out (flocculated) by the addition of sufficient quantities of inorganic electrolytes such as NaCl.

The sedimented polypyrrole latex obtained after centrifugation can, in principle, be dispersed in any solvent which is a good solvent for the adsorbed poly(vinylpyridine) stabilizer. In the case of the P4VP-BM only three solvents were found to be satisfactory: water, dilute mineral acid, and methanol (although not a solvent for neutral P4VP-BM, water is a solvent for the protonated copolymer). Qualitatively it seemed that the redispersal process was much more efficient for both the P4VP(II)- and (P4VP-BM)-stabilized latices than other stabilizers such as PVA; complete redispersal was obtained in all cases. This could prove to be a significant advantage in the large-scale production of polypyrrole latex.

The microanalytical data for various latex powders (see Table 2) indicated the presence of small but non-negligible quantities of iron. At present, it is unclear whether this is primarily due to iron-based dopant anions, iron complexation with the steric stabilizer, or physical encapsulation.

No analytical procedures for the quantitative determination of poly(vinyl pyridine)s were found in the literature. Initial studies on the supernatants using both infra-red and fluorescence techniques were unsuccessful. However, further work led to the development of a method based on laser Raman spectroscopy.

It is apparent from Table 2 that increasing the initial P4VP-BM stabilizer concentration from 4·5 g/l to 6·0 g/l has little or no effect on either the average particle diameter (D) or the mass of adsorbed stabilizer (M), at least within experimental error (some macroscopic precipitation was observed at a stabilizer concentration of 4·0 g/l, which suggests that both M and D were probably underestimated in this case). These results suggest a relatively constant thickness for the outer layer of P4VP-BM stabilizer, which is consistent with the narrow range of values of the compressed pellet conductivities. In contrast, previous workers have reported that, for PVA-stabilized polypyrrole latices, an increased stabilizer concentration leads to a larger adsorbed mass of stabilizer and a concomitant decrease in solid-state conductivity [7,9].

The S.E.M. studies suggest that it is reasonable to treat the latex particles as concentric spheres consisting of an inner conducting core and an insulating outer layer even in the solid state. Assuming a uniform coating of stabilizer over each polypyrrole particle, and using the data in Table 2, we estimate the average stabilizer layer thickness in the solid state to be approximately 3 ± 1nm. Thus, the conducting components within the latex pellet are separated by ∿60Å - rather a large distance for an electron-tunnelling mechanism. The relatively high observed conductivities cast some doubt over the validity of the assumptions inherent in this rather simplistic calculation. However, it is known that poly(vinyl pyridine)s can form semiconducting complexes with iron. If this were true of the adsorbed P4VP-BM stabilizer, the electron-tunnelling probability could be increased substantially.

Preliminary experiments on the redispersed, (P4VP-BM)-stabilized polypyrrole latex indicated that the destabilization induced by the addition of base could be reversed simply by the addition of excess acid. This weak, reversible flocculation behavior strongly suggests that destabilization is due to the reduced solvation and layer thickness of the deprotonated stabilizer (which is quickly restored on reprotonation) rather than actual desorption of the stabilizer from the latex particles (see Figure 4b). Our later quantitative studies (see Figure 2) show that there is a linear relationship between the latex particle concentration and the number of moles of hydroxide ion required to produce flocculation. From the experimental data we calculate that the mole ratio of hydroxide ion to pyridine rings at the onset of flocculation is approximately 1:1, which is consistent with complete deprotonation of the P4VP-BM stabilizer. We wish to emphasize that, since complete flocculation of the latex particles occurs under relatively acidic conditions (pH 3·6 ± 0·1), the undesirable deprotonation of polypyrrole at the ring nitrogen (which is known to cause a concomitant large decrease in conductivity [22-24]) can be avoided by simply not adding excess base.

All attempts to solution-cast uniform films from latex dispersions were disappointing. Brittle, poor quality films of very low conductivity were obtained, presumably due to the high glass-transition temperature (Tg ∿ 105°C as measured by differential scanning calorimetry) and low film-forming ability of the P4VP-BM stabilizer. It is possible that these problems could be overcome by spin-coating methods. Further experiments are in progress.

CONCLUSIONS

Spherical, sub-micronic polypyrrole latices can be prepared using poly(4-vinyl pyridine)-based steric stabilizers. The P4VP-BM copolymer was found to be particularly effective, promoting particle formation at relatively low concentrations. The use of such stabilizers allows the polypyrrole particles to be controllably and reversibly aggregated or stabilized, depending on the pH of the dispersion medium. The latices were characterized with respect to particle size, base-induced flocculation behavior and mass of adsorbed stabilizer.

Scanning electron microscopy studies indicate the polypyrrole particles retain their size and shape after pelletization of the dry latex powder. The solid-state conductivity of such pellets is surprisingly high (0·4 to 2·1 Scm^{-1}), despite the presence of the adsorbed layer of stabilizer surrounding each polypyrrole particle.

Future work will focus on the preparation and characterization of polypyrrole latices using analogous poly(2-vinyl pyridine)-based copolymers as steric stabilizers.

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REFERENCES

1. K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt and G. B. Street, J. Chem. Soc. Chem. Commun., 854 (1979).
2. A. F. Diaz and K. K. Kanazawa in "Extended Linear Chain Compounds" edited by J. S. Miller, 3, 417, Plenum Press, London (1983).
3. G. B. Street in "Handbook of Conducting Polymers" edited by T. A. Skotheim, p 265, Dekker, New York (1985).
4. R. B. Bjorklund and B. Liedberg, J. Chem. Soc. Chem. Commun., 1293 (1986).
5. A. Yassar, J. Roncali and F. Garnier, Polym. Commun., 28(4), 103 (1987).
6. S. P. Armes and B. Vincent, J. Chem. Soc. Chem. Commun., 288 (1987).
7. S. P. Armes, J. F. Miller and B. Vincent, J. Coll. Inter. Sci., 118(2), 410 (1987).
8. S. P. Armes, Ph.D. thesis, University of Bristol, U.K., (1987).
9. J. F. Miller, B.Sc. thesis, University of Bristol, U.K., (1987).

10. N. Cawdry, B.Sc. thesis, University of Bristol, U.K., (1988).

11. T. Obey, private communication.

12. A. Pron, Z. Kucharski, C. Budrowski, M. Zagorska, S. Krichene, J. Suivalski, G. Dehe and S. Lefrant, J. Chem. Phys., 83(11), 5923 (1985).

13. R. E. Myers, J. Electron. Mater., 2, 61 (1986).

14. G. P. Gardini and V. Bocchi, J. Chem. Soc. Chem. Commun., 148 (1986).

15. K. E. J. Barrett, "Dispersion Polymerization in Organic Media," John Wiley, London (1975).

16. D. H. Napper, "Polymeric Stabilization of Colloidal Dispersions," Academic Press, London (1983).

17. J. E. Armones, private communication.

18. J. B. Berkowitz, M. Yamin and R. M. Fuoss, J. Polym. Sci., 28, 69 (1958).

19. S. P. Armes, Synth. Met., 20(3), 367 (1987).

20. W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," Chapter 1, p 14-16, W. A. Benjamin, Inc., New York (1968).

21. P. Molyneux, "Water-soluble Synthetic Polymers: Properties and Behavior," volume 2, CRC Press, Florida (1983).

22. H. Munstedt, N. Naarman and G. Kohler, Mol. Cryst. Liq. Cryst., 118, 129 (1985).

23. H. Munstedt, Polymer, 27, 899 (1986).

24. O. Inganas, R. Erlandsson, C. Nylander, and I. Lundstrom, J. Phys. Chem. Solids, 45(4), 427 (1984).