

# Synthesis of Novel Polyaniline Colloids Using Chemically Grafted Poly(*N*-vinylpyrrolidone)-Based Stabilizers

C. DEARMITT AND S. P. ARMES<sup>1</sup>

*School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, BN1 9QJ, United Kingdom*

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We report the synthesis of polyaniline colloids using a new polymeric steric stabilizer based on a poly(*N*-vinylpyrrolidone) copolymer. This copolymer stabilizer contains pendant aniline groups which are believed to participate in the *in situ* aniline polymerization, leading to the chemical grafting of the stabilizer onto the surface of the polyaniline particles. The stabilizer is compatible with both  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{KIO}_3$  oxidants and so represents an improvement over our earlier work. Our electron microscopy studies have confirmed that the polyaniline colloid morphology depends on the oxidant used for the aniline polymerization. Thus the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidant produces spherical particles while the  $\text{KIO}_3$  leads to the formation of "rice-grain"-shaped particles. The mass ratio of grafted stabilizer/polyaniline has been indirectly determined by assaying postreaction supernatant solutions by colorimetry using congo red dye as a complexing agent. The polyaniline colloids were further characterized by a wide range of techniques including FTIR and visible absorption spectroscopy, microanalysis, dc conductivity, and thermogravimetric analysis. © 1992 Academic Press, Inc.

## INTRODUCTION

Polyaniline is generally recognized to be the only completely air-stable conducting polymer (1). It can be synthesized either chemically (2–4) or electrochemically (5–7) as a bulk powder or film. Although soluble in various solvents such as THF, DMF, or NMP in the undoped state, the doped (conducting) form is insoluble in most solvents (except concentrated acids (8)) and is therefore an intractable and unprocessable material. Various workers have attempted to improve the processability of polyaniline, usually by modifying the polymer chain with alkyl, alkoxy, or sulphonic groups (9–11).

Recently, one of us (S.P.A.) reported the preparation of sterically stabilized colloidal polyaniline particles via dispersion polymerization (12). The steric stabilizer was a poly(2-vinylpyridine-co-4-aminostyrene) random (statistical) copolymer. Since then we have reported the use of other stabilizers based on

poly(4-vinylpyridine) (13), poly(vinyl alcohol) (14), and poly(*N*-vinylimidazole) (15). The chemical oxidant used for the polymerization of aniline in all of these systems was  $\text{KIO}_3$ . Our attempts to use the more conventional  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidant in these studies were unsuccessful due to the formation of an insoluble complex between this oxidant and each of the stabilizers (12–15). We now report that a tailor-made poly(*N*-vinylpyrrolidone-co-4-aminostyrene) [PVP-AS] copolymer (see Fig. 1) is compatible with the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidant and that this stabilizer/oxidant combination also produces stable colloidal dispersions of polyaniline.

## EXPERIMENTAL

### (a) Preparation and Characterization of Steric Stabilizer

The PVP-AS steric stabilizer was prepared by bulk free-radical copolymerization of *N*-vinylpyrrolidone (kindly donated by General Aniline & Film Corp.) and 4-aminostyrene

<sup>1</sup> To whom correspondence should be addressed.

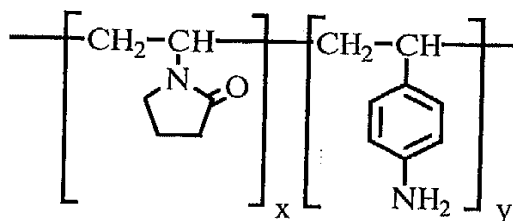


FIG. 1. Chemical structure of the poly(*N*-vinylpyrrolidone-co-4-aminostyrene) copolymer stabilizer.

(from Polysciences) for 47 h at 70°C at an initial comonomer mole ratio (N-VP/4-AS) of 17.5/1 using 2,2'-azobisisobutyronitrile. The resulting random copolymer was purified by precipitation into THF from aqueous solution and then freeze-dried from water overnight. Since the copolymer was insoluble in THF our molecular weight distribution data were obtained using aqueous GPC under the following conditions: polymer concentration, 0.2% (w/v); flow rate, 1.0 ml min<sup>-1</sup>; two PL aquagel-OH 40 columns; 0.2 M NaNO<sub>3</sub> + 0.01 M NaH<sub>2</sub>PO<sub>4</sub> eluent (pH 2); monodisperse PEG/PEO calibration standards; RI detector. These studies indicated an  $M_n$  of 44,000 and an  $M_w$  of 99,000 for the copolymer. An FTIR spectrum of the copolymer dispersed in a KBr disc contained bands at 1517, 1180, and 832 cm<sup>-1</sup> in addition to those due to the poly(*N*-vinylpyrrolidone) homopolymer. These bands were coincident with those in the reference compound 4-ethylaniline (16), indicating the presence of the polymerized 4-aminostyrene group. The relative copolymer composition was determined by <sup>1</sup>H NMR spectroscopy by comparing the aromatic peak integral due to the 4-aminostyrene group at  $\delta$  6–7 to the total polymer peak integral (d<sub>6</sub>-DMSO solvent, TMS reference). The copolymer was found to contain 2.4 mol% 4-aminostyrene groups by this method.

#### (b) Preparation of Polyaniline Colloids

(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.49 g) (or KIO<sub>3</sub> (0.46 g)) and PVP-AS (0.50–0.75 g) were dissolved together in 50 ml 1.2 M hydrochloric acid and this solution was then aged at 20°C for 30 min with

continuous stirring. Aniline monomer (0.50 ml) was then injected via syringe and the reaction mixture stirred for 20 h. The resulting dark green dispersions were centrifuged at 50,000 rpm for 2 h using a Beckman L2-65B ultracentrifuge. The supernatants were decanted and the sediments redispersed in 1.2 M HCl. The colloids were then filtered under gravity to remove undispersed sediment. These experiments were repeated with *N*-methylaniline monomer (0.50 ml) at the same oxidant/monomer mole ratio.

#### (c) Characterization of Polyaniline Colloids

(i) Visible absorption spectra of diluted, doped polyaniline and poly(*N*-methylaniline) dispersions were recorded using a Perkin-Elmer PU 8720 UV visible absorption spectrometer. A polyaniline film was cast on a CaF<sub>2</sub> disc from an aqueous colloidal dispersion. An IR spectrum of this film was recorded using a Perkin-Elmer FTS-40 instrument.

(ii) Transmission electron microscopy studies were made on dilute dispersions dried down on carbon-coated copper grids (from Bio-Rad) using a JEOL-100C instrument.

(iii) CHN and S elemental microanalyses were determined using a Perkin-Elmer 2400 instrument. Chlorine and iodine analyses were determined by the Schöniger oxygen combustion method.

(iv) Conductivity measurements were made at 20°C using conventional four-point probe techniques.

(v) Weight fractions of the as-prepared polyaniline dispersions and their respective supernatants (after centrifugation) were determined by drying to constant weight in a 60°C vacuum oven.

(vi) Thermogravimetric analyses of the dried conducting polymer films were determined using a Perkin-Elmer TGA-7 instrument.

(vii) The clear postcentrifugation supernatants were assayed for ungrafted PVP-AS

stabilizer by the following two colorimetric procedures.

The first method utilized congo red dye and was based on a modified procedure first described by Riedhammer (17). Briefly, 50  $\mu\text{l}$  of postreaction supernatant solution was added in turn to  $4 \times 10.0\text{-ml}$  aliquots of a  $0.10\text{ g dm}^{-3}$  stock solution of congo red in  $0.02\text{ M}$  NaOH (an alkaline stock solution was used to neutralize the acidic ( $\text{pH} \sim 0$ ) supernatant solution). Standard solutions containing 50  $\mu\text{l}$  of PVP-AS in  $1.2\text{ M}$  HCl at various (known) concentrations +  $10.0\text{-ml}$  congo red stock solution in  $0.02\text{ M}$  NaOH were used to construct a calibration curve. All visible absorption spectra were referenced to the congo red stock solution and were recorded immediately in  $10\text{-mm}$  cuvettes using the previously described spectrophotometer.

The second method utilized a  $\text{KI}/\text{I}_2/\text{citric acid}$  stock solution and was similar to that previously reported by us for the assay of poly(vinyl alcohol-co-vinyl acetate) copolymer in postreaction supernatant solutions of polypyrrole colloids using a  $\text{KI}/\text{I}_2/\text{boric acid}$  mixture (18). The analytical procedure adopted was identical to that described by Levy and Fergus (19).

(viii) A qualitative flocculation experiment was carried out as follows: one drop of a diluted polyaniline dispersion was added to  $10\text{ ml}$  of a  $1.0\text{ M}$   $(\text{NH}_4)_2\text{SO}_4$  solution at room temperature. Macroscopic precipitation (flocculation) of the colloid was observed immediately. The flocculated particles could be re-dispersed by dilution of the aqueous electrolyte solution followed by mechanical agitation.

## RESULTS AND DISCUSSION

Unlike our earlier poly(vinylpyridine)-based stabilizers, which exist as polyelectrolytes under the acidic conditions required for aniline polymerisation (12, 13), the nonionic nature of the PVP-AS stabilizer allows the use of the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidant for the preparation

of the polyaniline colloids. This oxidant is preferred to the  $\text{KIO}_3$  oxidant used in our earlier studies since the latter leads to the incorporation of substantial amounts of iodine (up to  $20\text{ wt}\%$ ) into both polyaniline colloids (13–15) and bulk powders (26). Thus this new formulation represents a significant improvement over our previous work (12–15). Vincent and co-workers have previously shown that the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidant can be used in conjunction with various polymeric stabilizers to prepare polyaniline colloids (20, 21). However the particle solids concentration obtained by these workers was always very low ( $0.1\text{--}0.2\%$ , w/v) compared to the present work ( $1.2\text{--}1.5\%$ , w/v). The minimum PVP-AS stabilizer concentration required to prepare stable colloidal dispersions is approximately  $10\text{ g/liter}$ ; lower concentrations resulted in the macroscopic precipitation of the conducting polymer. This stabilizer concentration is similar to that required for our previous copolymer stabilizers ( $7.5\text{--}10.0\text{ g/liter}$ ) (13–15).

The results of various reaction conditions for the preparation of sterically stabilized polyaniline dispersions are summarized in Table I. It is clear from the presented data that the PVP-AS stabilizer allows the use of both  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{KIO}_3$  oxidants for the preparation of such colloids and furthermore that the choice of oxidant appears to influence the polyaniline particle morphology. For example, samples 1–5 were all prepared using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and produced polydisperse spherical particles similar to those reported by Vincent and Waterson (20). On the other hand, sample 6, which was prepared under similar reaction conditions using the  $\text{KIO}_3$  oxidant, was composed of rice-grain-shaped particles (see Fig. 2a) similar to those dispersions reported by us in earlier papers (12–15). It appears that in some circumstances the particle morphology of colloidal polyaniline can be affected simply by the choice of the oxidant species. However, we wish to emphasize that these morphological changes are rather more subtle than they might seem at first. For ex-

TABLE I  
Reaction Conditions for the Preparation of Polyaniline Colloids

Sample number	Monomer species	Oxidant species	Initial stabilizer concentration (g/liter)	Reaction temperature (°C)	Particle morphology	Conductivity (S cm <sup>-1</sup> )
1	Aniline	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	10.0	19	Spheres (300–400 nm diameter)	0.2
2	Aniline	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	12.5	19	Spheres (300–400 nm diameter)	0.1
3	Aniline	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	15.0	19	Spheres (300–400 nm diameter)	0.1
4	Aniline	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	20.0	19	Spheres (300–400 nm diameter)	0.1
5	Aniline	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	10.0	30	Spheres (50–60 nm diameter)	0.4
6	Aniline	KIO <sub>3</sub>	15.0	19	Polydisperse rice grains	—
7	N-Methylaniline	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	15.0	19	Spheres (200–300 nm diameter)	~10 <sup>-4</sup>

ample, while the KIO<sub>3</sub> oxidant apparently always leads to the formation of rice-grain- or needle-shaped particles (12–15), *both* spherical *and* rice-grain morphologies have been observed when using the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidant with various polymeric stabilizers (20, 21). The overall particle morphology is presumably controlled by both the kinetics of the aniline polymerization and the grafting efficiency of the steric stabilizer. These two processes will be influenced by various parameters such as the type of oxidant and steric stabilizer, solution viscosity, stabilizer aging time, and catalytic impurities. We have commenced a study of the kinetics of colloidal particle formation by <sup>1</sup>H NMR spectroscopy and these results will be communicated in a future publication (22).

Using the PVP-AS stabilizer/(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidant system we generally observed polydisperse spherical particles in the size range 300–400 nm diameter (see sample 4 in Fig. 2b). In one instance (sample 5, see Fig. 2c) we observed smaller, flocculated particulates. We do not have any satisfactory explanation for these observed particle morphologies at the present time. However, our sedimentation observations are consistent with these morphologies so we do not believe they result simply from some artifact of the drying down process. For example, sample 4 was much more easily sedimented by centrifugation (50,000 rpm for 5 m) than sample 5 (25,000

rpm for 18 h), which is fully consistent with these samples' respective apparent particle sizes obtained from electron microscopy.

We have recently described a novel particle size analysis technique based on charge-velocity analysis (23). Analysis of sample 3 by this method indicated an upper limit average particle diameter of approximately 100 nm (24). This result suggests that the large spherical polyaniline particles observed in our TEM studies are actually comprised of loosely aggregated clusters of smaller primary particles that undergo fragmentation under the extreme conditions of the charge-velocity analysis experiment.

There are at least two plausible mechanisms by which these particulate aggregates may be formed. First, the primary particles may not be completely covered by the grafted copolymer stabilizer; this would lead to particle aggregation via a bridging flocculation mechanism. A second possibility could be interparticle cross-linking reactions between the adsorbed steric stabilizer layers. These could occur in principle via the coupling of oxidized, ungrafted pendant aniline groups. There is also some evidence to suggest that the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidant in the reaction solution may cause cross-linking between the pyrrolidone rings of the copolymer stabilizer (25).

The PVP-AS stabilizer can also be used to produce sterically stabilized poly(*N*-methylaniline) colloids. Spherical particles in the size

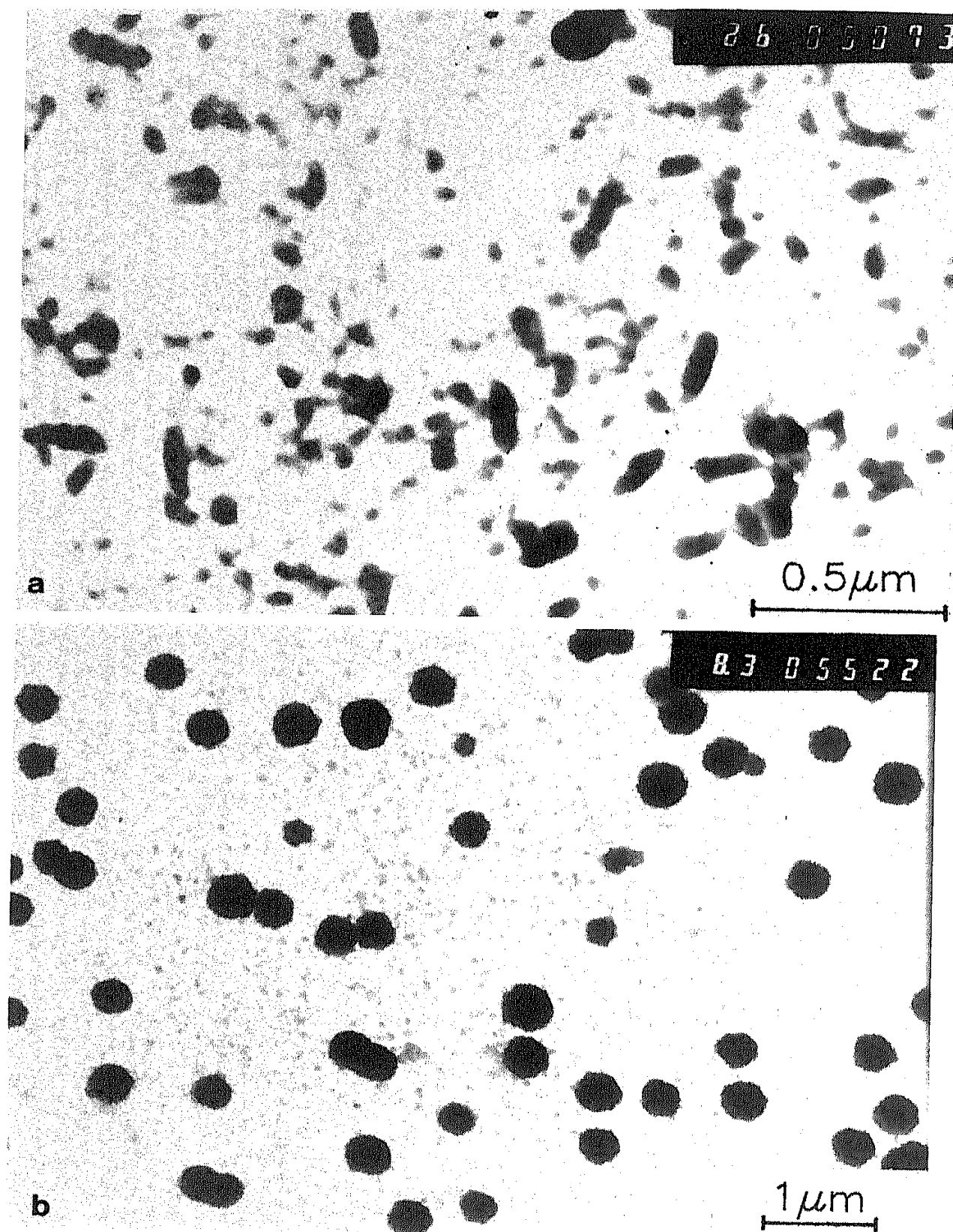


FIG. 2. Transmission electron micrographs of sterically stabilized conducting polymer colloids. (a) Polyaniline sample 6, (b) polyaniline sample 4, and (c) polyaniline sample 5.

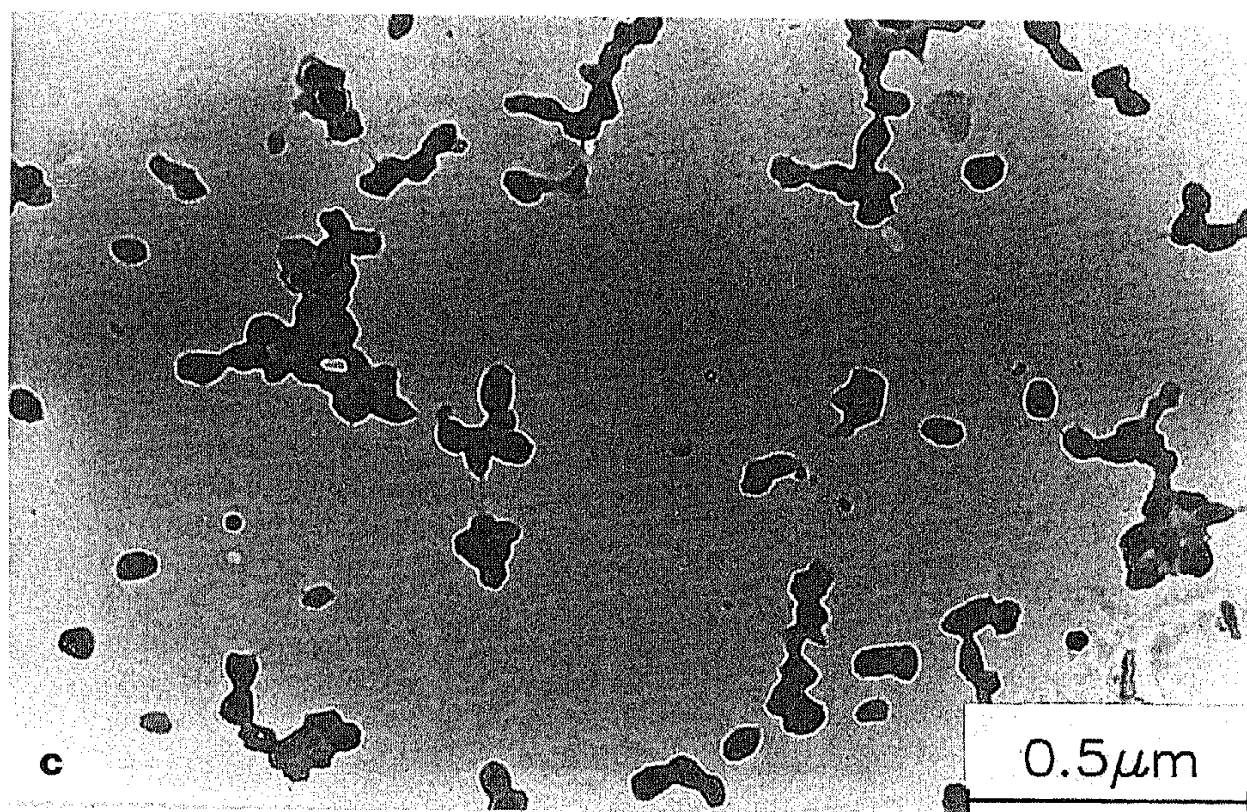


FIG. 2.—Continued

range 200–300 nm diameter are produced with the  $\text{KIO}_3$  oxidant.

The visible absorption spectra of diluted, doped polyaniline and doped poly(*N*-methylaniline) dispersions are shown together in Fig. 3. These spectra are similar to those reported by Watanabe and co-workers for electrochemically synthesized polyaniline and poly(*N*-methylaniline) films (26).

Thermogravimetric analyses of bulk polyaniline, colloidal polyaniline, and colloidal poly(*N*-methylaniline) are shown in Fig. 4. As expected, the colloidal polyaniline is marginally less stable than the bulk powder sample due to the increased surface area of the former. The poly(*N*-methylaniline) colloid appears to have enhanced thermal stability relative to the polyaniline colloids.

Microanalyses of the polyaniline colloids were generally satisfactory. Those prepared with the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidant contained chlorine and sulfur (as chloride and sulfate dopant anions, respectively (2)), while those prepared

with the  $\text{KIO}_3$  oxidant contained chlorine and iodine (as chloride and various iodine species, respectively (27)).

An FTIR spectrum of a polyaniline colloid film is shown in Fig. 5. This spectrum is very similar to that of chemically or electrochemically synthesized polyaniline films (28, 29) except for the presence of an additional absorbance peak at  $1650\text{ cm}^{-1}$  (see arrow) due to the pyrrolidone ring carbonyl group of the copolymer stabilizer. Thus the incorporation of the copolymer stabilizer into the polyaniline particles is confirmed, albeit only qualitatively.

The  $\text{KI}/\text{I}_2$ /citric acid colorimetric method has been used by Levy and Fergus to assay aqueous solutions for poly(*N*-vinylpyrrolidone) homopolymer (19). Unfortunately this approach was found to be unsuitable for the assay of the PVP-AS copolymer used in the present work. This was because the iodine component of the calibration solution unexpectedly oxidized the copolymer's pendant aniline groups during the analysis. Thus, the



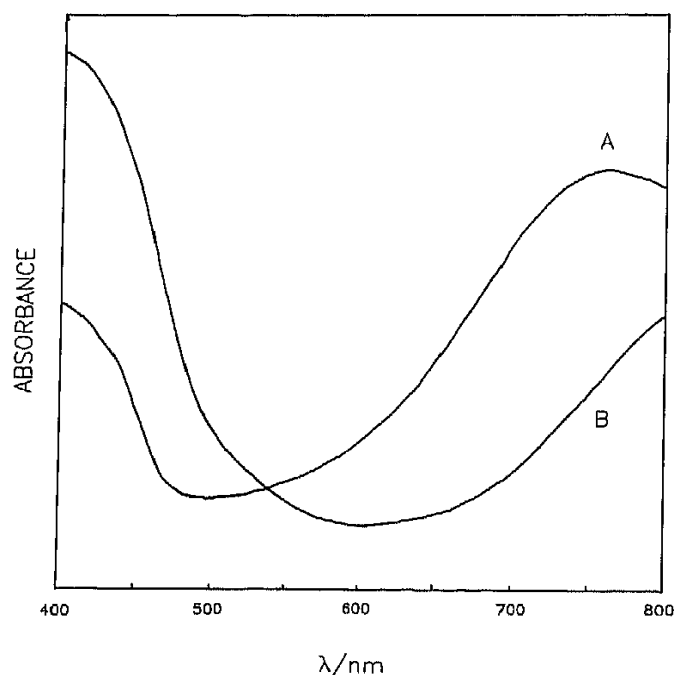


FIG. 3. Visible absorption spectra of (A) doped polyaniline and (B) poly(*N*-methylaniline) colloids.

visible absorption peak due to the copolymer-iodine complex at 500 nm was quickly obscured by growing absorption peaks at 414 and 540 nm due to the anilinium radical-cation species generated by this oxidation side reaction (13, 14).

In contrast, the congo red dye is chemically unreactive toward the copolymer's aniline groups and therefore this method can be used to determine the concentration of the ungrafted copolymer in the postreaction supernatant solution. The results of our copolymer stabilizer assays for samples 1–4 are shown in Fig. 6. Increasing the initial stabilizer concentration leads to a corresponding increase in the proportion of grafted stabilizer per unit mass of polyaniline. Taking into account the solids content of both the as-made dispersion and the corresponding supernatant (as determined by gravimetry), we calculate that the polyaniline dispersions contain up to 43 wt% of the copolymer stabilizer. Simple calculations based on the congo red assay of the supernatant of sample 5 suggest a stabilizer adsorption mass per unit area of approximately  $7 \text{ mg m}^{-2}$ . This value is rather higher than

that calculated for a poly(vinyl alcohol-co-vinyl acetate) steric stabilizer that was physically adsorbed onto polypyrrole colloids ( $3 \text{ mg m}^{-2}$ ) (18). However, the chemical grafting of the PVP-AS stabilizer used in the present work probably results in a more compact outer layer of solvated, adsorbed stabilizer compared to a stabilizer that is merely physically adsorbed.

Although our flocculation experiment was only qualitative in nature, the observation of reversible colloidal aggregation has significant implications. Previous workers have shown that poly(*N*-vinylpyrrolidone) homopolymer is precipitated from aqueous solution at room temperature by the addition of  $(\text{NH}_4)_2\text{SO}_4$  electrolyte (30). Thus, the particle aggregation that results from the addition of colloidal polyaniline to a  $1.0 \text{ M}$   $(\text{NH}_4)_2\text{SO}_4$  solution strongly suggests that at least some of the grafted PVP-AS copolymer is on the outside of the polyaniline particles. Furthermore, the ionic strength of the aniline polymerization medium ( $1.2 \text{ M}$  HCl) is far too high to allow effective charge stabilization of the particles. Hence this adsorbed copolymer must be responsible for the colloidal stability of the as-made polyaniline dispersion via a steric stabilization mechanism (31). The observation of reversible flocculation further suggests that the copolymer stabilizer is not desorbed from the polyaniline particles during the aggregation process. This is fully consistent with our hypothesis that the stabilizer is actually chemically grafted (rather than merely physically adsorbed) onto the particle surface.

The solid-state conductivities of compressed pellets or cast films fabricated from these polyaniline colloids lie in the range  $0.1\text{--}0.4 \text{ S cm}^{-1}$  (see Table I) and hence are similar to those reported for other sterically stabilized polyaniline dispersions (12–15, 20–22). Such conductivities are remarkable in view of the adsorbed layer of insulating copolymer stabilizer which must completely coat each polyaniline particle in order to account for the long-term colloidal stability of the dispersions. The conductivity of the poly(*N*-methylaniline) colloid is  $1 \times 10^{-4} \text{ S cm}^{-1}$ , which is an

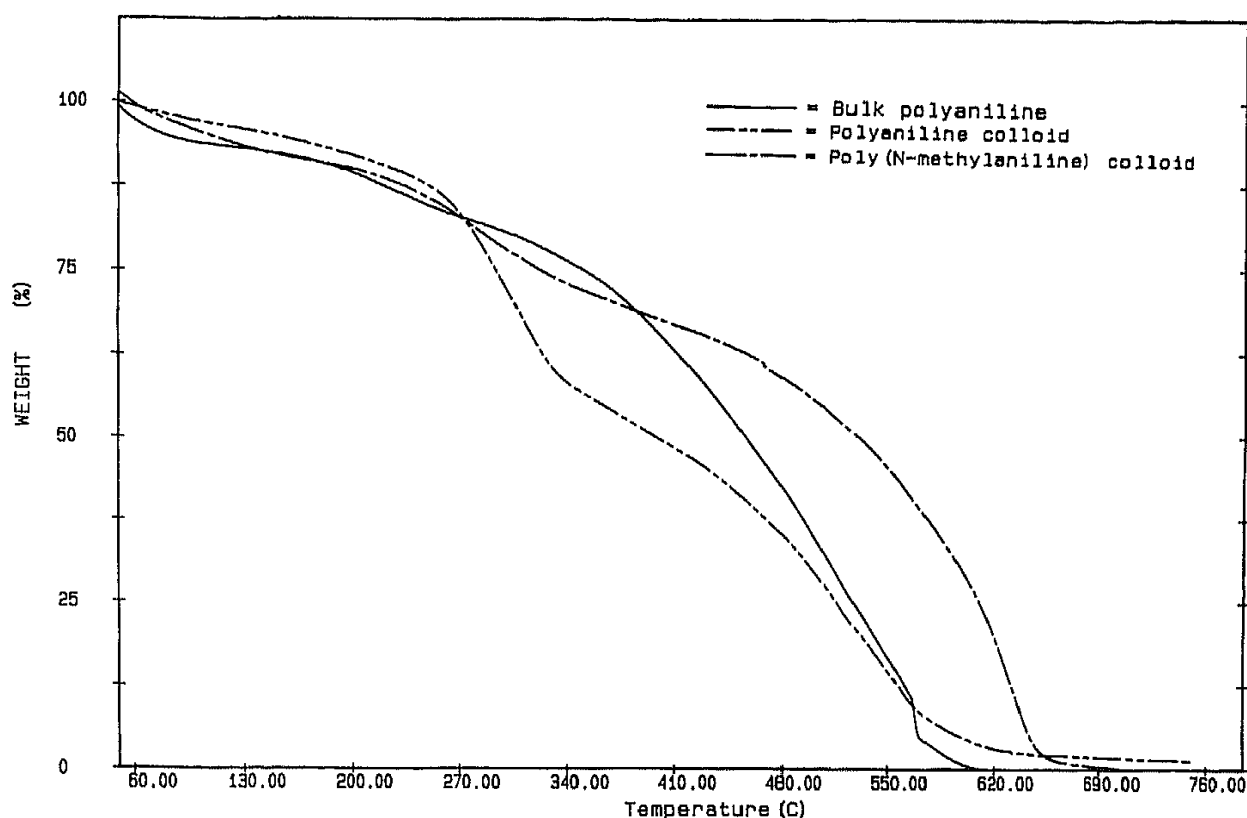


FIG. 4. Thermogravimetric analyses of bulk polyaniline, polyaniline colloid, and poly(*N*-methylaniline) colloid.

order of magnitude lower than that reported for electrochemically synthesized poly(*N*-methylaniline) films (32).

### CONCLUSIONS

We have synthesized and characterized a random copolymer based on poly(*N*-vinylpyrrolidone) which contains 2.4 mol% pen-

dant aniline groups and have shown it to be an effective steric stabilizer for polyaniline colloids. This copolymer represents an improvement over previously reported stabilizers since it is compatible with the preferred oxidant for aniline polymerizations, namely,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , as well as the previously reported  $\text{KIO}_3$  oxidant.

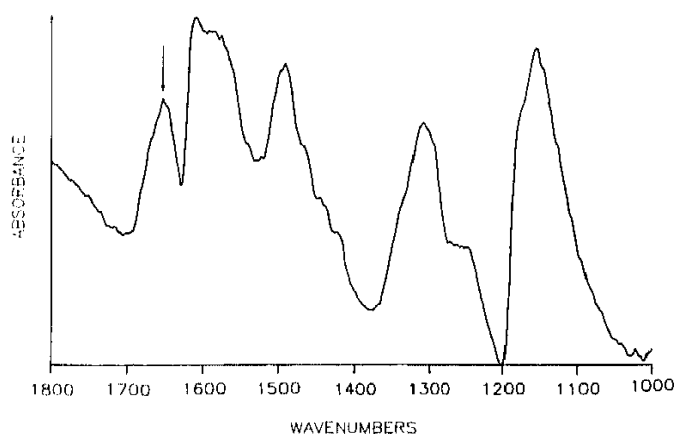


FIG. 5. FTIR spectrum of a polyaniline colloid film (sample 5).

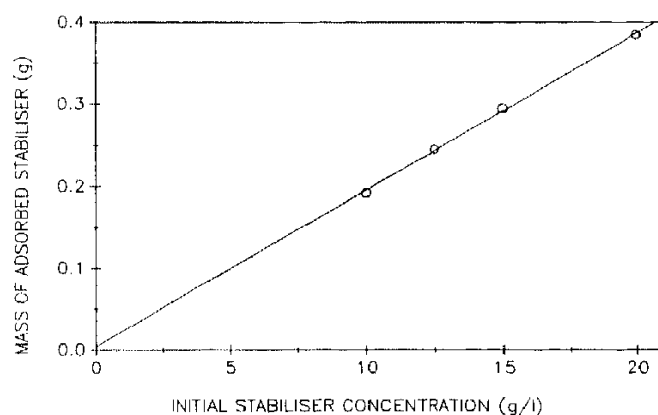


FIG. 6. Mass of PVP-AS stabilizer adsorbed onto colloidal polyaniline particles as a function of the initial solution concentration of stabilizer.



The particle morphology of these colloids depends on the oxidant used for the aniline polymerization. The  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  oxidant produced spherical particles, whereas the  $\text{KIO}_3$  oxidant produced polydisperse rice-grain particles.

An absorption peak at  $1650\text{ cm}^{-1}$  in the FTIR spectrum of these polyaniline dispersions confirms, albeit qualitatively, the presence of the grafted copolymer stabilizer. The copolymer stabilizer/polyaniline mass ratio can be easily quantitatively determined by assaying the postreaction supernatant for ungrafted stabilizer. The solid-state dc conductivity of the colloidal polyaniline films or compressed pellets lie in the range  $0.1\text{--}0.4\text{ S cm}^{-1}$ , despite the presence of the insulating stabilizer component.

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#### REFERENCES

- See, for example, the conference proceedings of the ICSM 1988, published in *Synth. Met.* **27-29** (1989), and references therein.
- Armes, S. P., and Miller, J. F., *Synth. Met.* **22**, 385 (1988).
- Pron, A., Genoud, F., Menardo, C., and Nechtschein, M., *Synth. Met.* **24**, 193 (1988).
- Chiang, J. -C., and MacDiarmid, A., *Synth. Met.* **13**, 193 (1986).
- McManus, P. M., Yang, S. C., and Cushman, R. J., *J. Chem. Soc. Chem. Commun.* 1556 (1986).
- Lacroix, J. C., Kanazawa, K. K., and Diaz, A., *J. Electrochem. Soc.* **136**(5), 1308 (1989).
- Watanabe, A., Mori, K., Iwaski, Y., Murakami, S., and Nakamura, Y., *J. Polym. Sci. Polym. Chem. Ed.* **27**, 4431 (1989).
- Cao, Y., Andreatta, A., Heeger, A. J., and Smith, P., *Polymer* **30**, 2305 (1989).
- Ni, S., Wang, L., Wang, F., and Shen, L., *Polym. Commun.* **30**, 123 (1989).
- MacInnes, D., and Funt, B. L., *Synth. Met.* **25**, 235 (1988).
- Kallitsis, J., Koumanakos, E., Dalas, E., Sakkopoulos, S., and Koutsoukos, P. G., *J. Chem. Soc. Chem. Commun.* 1146 (1989).
- Armes, S. P., and Aldissi, M., *J. Chem. Soc. Chem. Commun.* 88 (1989).
- Armes, S. P., Aldissi, M., Agnew, S. F., and Gottesfeld, S., *Langmuir*, in press.
- Armes, S. P., Aldissi, M., Agnew, S. F., and Gottesfeld, S., *Mol. Cryst. Liq. Cryst.* **190**, 63 (1990).
- Bay, R. F. C., Armes, S. P., Pickett, C., and Ryder, K., *Polymer* **32**, 2456 (1991).
- "The Aldrich Library of F.T.I.R. spectra" (C. J. Pouchert, Ed.), 1st ed., Vol. 1, p. 1202, 1985.
- Riedhammer, T. M., *J. Assoc. Off. Anal. Chem.*, **62**(1), 52 (1979).
- Armes, S. P., Miller, J. F., and Vincent, B., *J. Colloid Interface Sci.* **118**(2), 410 (1987).
- Levy, G. B., and Fergus, D., *Anal. Chem.* **25**(9), 1408 (1953).
- Vincent, B., and Waterson, J., *J. Chem. Soc. Chem. Commun.* 683 (1990).
- Cooper, E. C., and Vincent, B., *J. Phys. D* **22**, 1580 (1989).
- DeArmitt, C., and Armes, S. P., in preparation.
- Armes, S. P., Aldissi, M., Idzorek, G. C., Keaton, P. W., Rowton, L. J., Stradling, G. L., Collopy, M. T., and McColl, D. B., *J. Colloid Interface Sci.* **141**(1), 119 (1991).
- Armes, S. P., Idzorek, G. C., and Stradling, G. L., unpublished results.
- Anderson, C. C., Rodriguez, F., and Thurston, D. A., *J. Appl. Polym. Sci.* **23**, 2453 (1979).
- Watanabe, A., Mori, K., Iwabuchi, A., Iwasaki, Y., Nakamura, Y., and Ito, O., *Macromolecules* **22**, 3521 (1989).
- Armes, S. P., and Aldissi, M., *Polymer* **32**, 2043 (1991).
- Tang, J., Jing, X., Wang, B., and Wang, F., *Synth. Met.* **24**, 231 (1988).
- Sariciftci, N. S., Bartonek, M., Kuzmany, H., Neugebauer, H., and Neckel, A., *Synth. Met.* **29**, 193 (1989).
- Jirgensons, B., *J. Polym. Sci.* **8**, 519 (1952).
- Barrett, K. E. J., "Dispersion Polymerisation in Organic Media," Wiley, London, 1975.
- Comisso, N., Daolio, S., Mengoli, G., Salmaso, R., Zecchin, S., and Zotti, G., *J. Electroanal. Chem.* **255**, 97 (1988).