

Poly(1-vinylimidazole-co-4-aminostyrene): steric stabilizer for polyaniline colloids

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We report the preparation and characterization of polyaniline colloids using a new steric stabilizer based on poly(1-vinylimidazole). This stabilizer contains pendant aniline units which participate in the aniline polymerization, resulting in the formation of sterically stabilized polyaniline particles which have a non-spherical 'rice-grain' morphology. It is shown that this form of polyaniline is more processable than the bulk powder that is normally obtained from a conventional chemical synthesis. The solid-state conductivity of solution-cast films or compressed pellets of these dispersions is reasonably high ($\sim 1 \times 10^{-2} \text{ S cm}^{-1}$), despite the presence of the insulating outer layer of chemically grafted stabilizer. We have characterized these polyaniline colloids using various techniques including electron microscopy, cyclic voltammetry, visible absorption and Fourier transform infra-red spectroscopy.

(Keywords: polyaniline; colloids; characterization)

INTRODUCTION

Recently one of us (S.P.A.) has described the preparation of novel colloidal dispersions of polyaniline¹⁻⁴. In these systems particle aggregation is prevented by a 'steric stabilization' mechanism. We have reported on the use of two polymeric surfactants as steric stabilizers: a tailor-made poly(vinylpyridine)-based random copolymer¹⁻³ and a derivatized poly(vinyl alcohol-co-vinyl acetate) copolymer^{2,4}. Both these surfactants contain pendant aniline units which, we believe, participate in the *in situ* aniline polymerization, resulting in the chemical grafting of the surfactant to the polyaniline particle surface². Electrically conductive thin films can be easily fabricated from aqueous dispersions of these polyaniline colloids; thus such systems significantly improve the processability of the normally intractable electroactive components.

We have further shown that the nature of the adsorbed steric stabilizer can influence the physical properties of these polyaniline colloids. For example, poly(vinyl alcohol-co-vinyl acetate)-based stabilizers produce colloids with good film-forming properties⁴ whereas poly(vinylpyridine)-stabilized colloids exhibit reversible base-acid flocculation-stabilization behaviour³.

In the present paper we report the preparation and characterization of polyaniline colloids using a new tailor-made steric stabilizer, namely poly(1-vinylimidazole-co-4-aminostyrene) (PVIMZ-AS) (Figure 1).

EXPERIMENTAL

Preparation and characterization of the copolymer stabilizer

The PVIMZ-AS copolymer was synthesized by free-radical precipitation polymerization of 1-vinylimidazole (ex. Aldrich) and 4-aminostyrene (ex. Poly-

sciences) at an initial comonomer mole ratio of 8.6:1 at $\sim 70^\circ\text{C}$ in benzene using 2,2'-azobisisobutyronitrile as an initiator. Both monomers were vacuum distilled and stored at -20°C in the absence of light prior to use. The resulting statistical copolymer was purified by precipitation from methanol, and dried at 0.13 Pa for at least 16 h prior to characterization by Fourier transform infra-red (FTi.r.; KBr disc) and ¹H nuclear magnetic resonance (n.m.r.; d₆-DMSO solvent, TMS reference) spectroscopy, gel permeation chromatography (g.p.c.) and microanalysis.

Aqueous g.p.c. was used to characterize the molecular weight of the PVIMZ-AS copolymer using two PL aquagel-OH 40 columns (Polymer Laboratories) and a 0.2 M NaNO₃/0.01 M NaH₂PO₄ (pH 2) eluent.

Preparation of polyaniline colloids

PVIMZ-AS copolymer (0.20–1.0 g) was dissolved in 100 ml 1.2 M HCl in a 150 ml screw-cap bottle with magnetic stirring at room temperature. Solid potassium iodate (KIO₃, 0.90 g) was added to this solution and the reaction mixture allowed to age for 10–80 min at room temperature with continuous stirring. After this period aniline monomer (1.00 ml) was injected via a syringe. The solution gradually darkened and turned blue over a period of a few minutes and eventually turned dark green, which is characteristic of doped polyaniline. This reaction mixture was then stirred for at least 24 h at room temperature (if the initial stabilizer concentration was

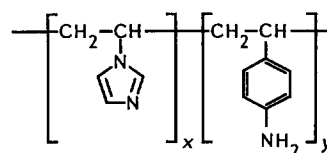


Figure 1 Chemical structure of the poly(1-vinylimidazole-co-4-aminostyrene) statistical copolymer

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Table 1 Reaction conditions for the preparation of polyaniline colloids

Sample no.	Stabilizer concentration (g l ⁻¹)	Ageing time (min)	Result
1	2.0	60	Precipitate
2	3.5	60	Fine precipitate
3	4.4	60	Fine precipitate
4	5.0	10	Colloid
5	10.0	80	Colloid

insufficient, macroscopic precipitation of polyaniline was observed within 2 h of the addition of aniline monomer).

The resulting colloidal dispersion was filtered under gravity and then centrifuged for ~10 h at 11 500 rev min⁻¹ using an MSE 25 I centrifuge. The dark green sediment was redispersed in 1.2 M HCl and then filtered under gravity. The results of the attempted preparations of polyaniline colloids are summarized in *Table 1*.

Characterization of the polyaniline colloids

Particle size and film morphology. The diluted dispersion was allowed to dry on a carbon-coated copper EM grid. This sample was examined by transmission electron microscopy (TEM) using a Jeol 100-C instrument. Coherent films of polyaniline were solution-cast under ambient conditions onto glass or Teflon substrates from more concentrated dispersions (typically 0.5–1.0 w/v%). These films were sputter-coated with a gold overlay and examined using an ASID-4D ultra-high resolution scanning attachment to the Jeol 100-C electron microscope.

Conductivity measurements. These were performed on thin films of polyaniline by conventional four-point probe techniques using a probe in the collinear configuration. The polyaniline samples were prepared by using the method described above.

Microanalysis. Microanalyses of the dried colloidal polyaniline film or powder were carried out using a Perkin Elmer 2400 microanalyser.

Spectroscopic characterization. An FTi.r. spectrum of the polyaniline colloid (sample 5) was recorded using a Nicolet 740 IR-PLAN Spectratech microscope. Visible absorption spectra of both the stable, doped polyaniline colloid and the flocculated, dedoped polyaniline colloid were recorded in HCl and NH₄OH solutions, respectively, using a PU 8720 instrument.

Cyclic voltammetry studies. Thin films of colloidal polyaniline were solution-cast onto a Pt disc. Single scan cyclic voltammograms were recorded in 10 M HCl solution at a scan rate of 100 mV s⁻¹ with an Ag/AgCl reference electrode using an EG & G model 273 potentiostat.

Thermal stability studies. Thermograms of both a solution-cast polyaniline colloid film (sample 5) and bulk polyaniline powder (prepared under identical conditions in the absence of the PVIMZ-AS stabilizer) were recorded using a Perkin-Elmer TGA-7 thermogravimetric analyser.

RESULTS AND DISCUSSION

Copolymer stabilizer

The incorporation of the 4-aminostyrene monomer into the copolymer was confirmed by FTi.r. spectroscopy (KBr disc) with additional bands being observed at 1179, 1279, 1450 and 1517 cm⁻¹ relative to a poly(1-vinylimidazole) homopolymer sample. All of these bands are found in the i.r. spectrum of 4-ethylaniline, which was used as a model compound for the polymerized 4-aminostyrene group⁵.

The ¹H n.m.r. spectrum of the copolymer has a peak at $\delta \approx 4.8$ due to the NH₂ protons of the 4-aminostyrene group. The integral of this peak was ratioed to the total polymer peak integral (all aliphatic and aromatic protons of both monomer units). On this basis it was estimated that the copolymer contained ~60 mol% 1-vinylimidazole units.

Aqueous g.p.c. analysis of the copolymer indicated a weight-average molecular weight of ~47 300. However, this analysis should be treated with some caution since the lower molecular weight tail of the copolymer was only partially eluted⁶.

Nitrogen microanalyses of the copolymer were intermediate between reported nitrogen microanalyses for poly(1-vinylimidazole)⁷ and poly(4-aminostyrene)⁸ homopolymers, respectively. Simple calculations indicate a 1-vinylimidazole:4-aminostyrene mole ratio of 60:40, which is consistent with the results obtained from ¹H n.m.r. spectroscopy. The CHN total microanalyses also suggested that the PVIMZ-AS copolymer contained ~8% H₂O (a water peak was observed in the copolymer n.m.r. spectrum). No allowance for this water content was made when weighing the stabilizer for the colloid syntheses (*Table 1*).

Polyaniline colloids

It is clear from the data in *Table 1* that the minimum PVIMZ-AS stabilizer concentration for the preparation of polyaniline colloids under the stated reaction conditions is 4.5–5.0 g l⁻¹. Lower stabilizer concentrations fail to prevent particle aggregation which leads in turn to the macroscopic precipitation of polyaniline. Such precipitates were not characterized further in this study. We have previously shown, using visible absorption spectroscopy, that the pendant aniline groups on other copolymer stabilizers are activated (oxidized) to anilinium radical cations by KIO₃ during the pre-polymerization ageing period^{3,4}. We believe that these moieties inevitably participate in the subsequent *in situ* aniline polymerization and thus lead to the chemical grafting of the copolymer to the polyaniline surface. Our visible absorption spectroscopy studies on the aged PVIMZ-AS/ KIO₃ solution prior to addition of aniline monomer indicate that the 4-aminostyrene groups (essentially pendant aniline groups) are similarly oxidized, with an absorption peak appearing at ~520 nm. Thus we believe that this copolymer is also chemically grafted onto the polyaniline particles rather than being merely physically adsorbed. One of us (S.P.A.) has previously shown that the extent of oxidation of the 4-aminostyrene groups in a poly(2-vinyl pyridine-co-4-aminostyrene) stabilizer by KIO₃ increases monotonically with ageing time⁹. Thus it is expected that longer ageing periods would generally increase the grafting efficiency of such stabilizers onto polyaniline particles. It is likely

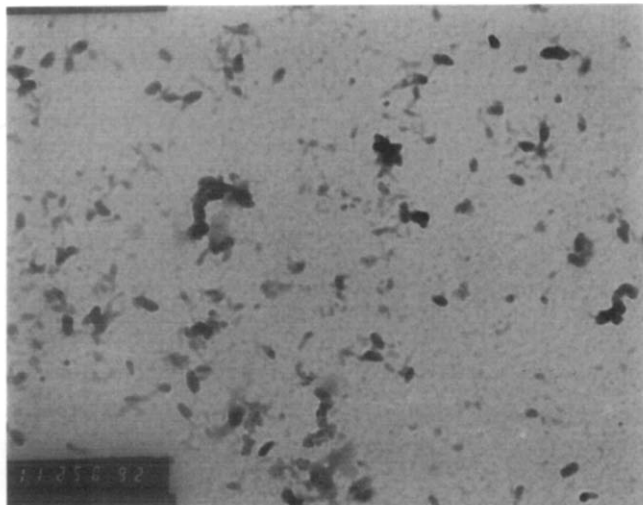


Figure 2 Transmission electron micrograph of a dried-down colloidal dispersion of polyaniline particles (sample 5). Magnification $\times 27\,000$

that the minimum stabilizer concentration could be reduced by increasing the ageing time. However, there are insufficient data in *Table 1* to allow us to draw such conclusions in the present study. It is noteworthy that very long ageing times (~ 24 h) lead to the precipitation of the PVIMZ-AS copolymer, presumably due to dimerization crosslinking reactions between the anilinium radical cations.

Previously we have reported^{1,3} that $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is an inappropriate oxidant for the preparation of polyaniline colloids using poly(vinylpyridine)-based steric stabilizers. This oxidant-stabilizer system led to the immediate formation of an insoluble complex prior to the addition of the aniline monomer. However, we found that the KIO_3 oxidant was compatible with such stabilizers and, as a consequence, it became the oxidant of choice for colloidal polyaniline syntheses. This work in turn led to an extensive study of the use of KIO_3 in the synthesis of bulk polyaniline powders¹⁰. In the present study we found that the PVIMZ-AS stabilizer was similarly incompatible with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and compatible with KIO_3 . One disadvantage in using KIO_3 is that it is reduced to iodide ions and/or free iodine during the aniline polymerization. These by-products are usually incorporated into the polyaniline colloids at relatively high levels (10–20 wt%)^{3,4}.

The TEM studies revealed a polydisperse 'rice-grain' morphology similar to that previously reported for polyaniline colloids^{1,3,4}. The particles were 60–360 nm long and 30–60 nm wide (*Figure 2*).

Our previous attempts to examine the morphology of colloidal polyaniline films by scanning electron microscopy (SEM) failed to detect the presence or absence of the individual 'rice-grain' particles⁹. This was probably due to the low resolution of the instrument (a Camscan II model). A scanning electron micrograph of a polyaniline film fabricated from sample 5 is shown in *Figure 3*. The improved resolution of the ASID-4D instrument clearly reveals the presence of the 'rice-grain' particles in the film. The particles appear to form thin strands in the solid state, giving rise to an overall fibrillar morphology similar to that previously reported for electrochemically synthesized polyaniline films¹¹. The average fibril width is comparable to the individual

particle width observed in the transmission electron micrographs but the average length of the fibrils is rather longer than the individual particle lengths. This suggests that the fibrils are formed from the end-on coalescence of the polyaniline rice-grains during the drying process.

The solid-state electrical conductivity of these colloidal polyaniline films is $0.02\text{--}0.04\text{ S cm}^{-1}$, which is approximately an order of magnitude lower than that of the polyaniline colloids previously reported^{1,3,4}. It is likely that the lower conductivity is due to more efficient stabilizer adsorption onto the polyaniline particles, which would be expected in view of the rather higher concentration of pendant aniline groups per stabilizer chain in the present study (40 mol% as opposed to $0.5\text{--}14.7\text{ mol}\%$). A higher proportion of insulating polymeric stabilizer in the polyaniline films would undoubtedly account for the reduced conductivity of these composites.

Our preliminary cyclic voltammetry studies suggest that this lower conductivity does not detract from the electrochemical cycling of the colloidal polyaniline films. A typical single scan cyclic voltammogram is shown in *Figure 4* and is essentially identical to those previously reported by ourselves^{3,4} and other workers^{12–14}. Thus colloidal polyaniline films could in principle be used in many of the suggested applications of conventional polyaniline films and the former system would clearly possess some advantages in terms of processability.

Typical microanalyses for the (PVIMZ-AS)-stabilized polyaniline colloids are: C 43.68%, H 4.73%, N 9.54%, Cl 12.49%, I 24.79% and O (by difference) 4.77%. This chemical composition is similar to that reported for other sterically stabilized polyaniline colloids^{3,4}. The visible absorption spectra for the stable, doped colloidal dispersion (pH ~ 0) and the flocculated, dedoped suspension (pH ~ 10) are identical to electrochemically or chemically prepared macroscopic polyaniline films subjected to the same acid or base treatments^{15,16}. The FTi.r. spectrum of the doped polyaniline colloid is shown in *Figure 5*. The bands at 1178 and 1507 cm^{-1} and the shoulder at $\sim 1600\text{ cm}^{-1}$ are due to the adsorbed PVIMZ-AS stabilizer, otherwise the spectrum is identical to that of bulk polyaniline films or powders prepared by conventional methods.

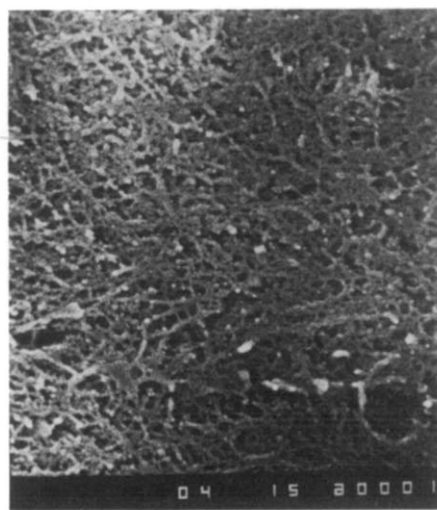


Figure 3 Scanning electron micrograph of an electrically conductive solution-cast film of colloidal polyaniline (sample 5). Magnification $\times 16\,900$

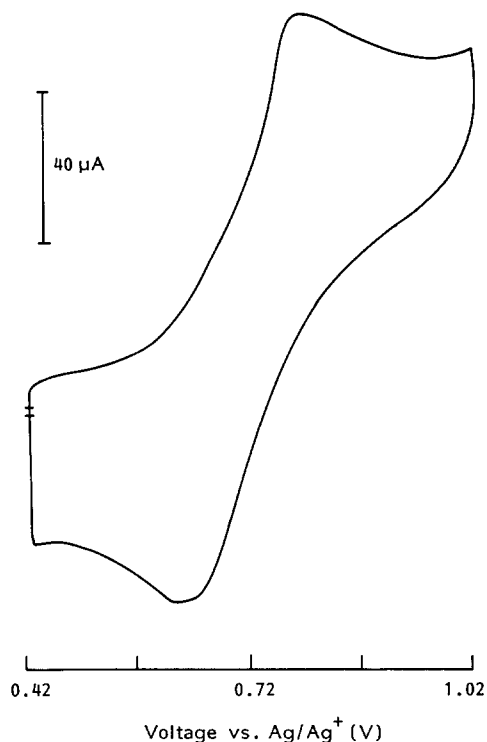


Figure 4 Single scan cyclic voltammogram of a solution-cast polyaniline film (sample 5) deposited on a platinum electrode in HCl

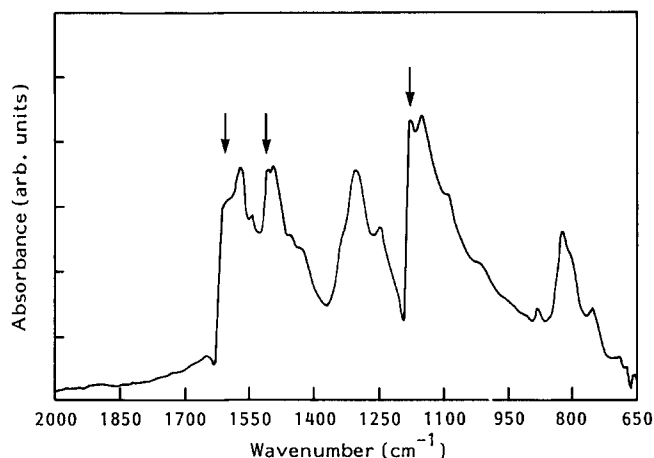


Figure 5 Fourier transform infra-red spectrum of doped polyaniline colloid

Our initial experiments have confirmed that the PVIMZ-AS stabilizer can be used with the KIO_3 oxidant to prepare colloidal dispersions of poly(*N*-methylaniline) as well as polyaniline¹⁷. Transmission electron microscopy indicates that the particles have a polydisperse spherical morphology, which suggests that the morphology of such sterically stabilized colloids is an intrinsic property of the electroactive component and is not strongly influenced by the nature of the oxidant or steric stabilizer.

Typical thermograms of colloidal polyaniline (sample 5) and bulk polyaniline powder (KIO_3 oxidant) are shown in Figure 6. The samples do not exhibit good thermal stability characteristics, with monotonic weight loss occurring over the whole temperature range. The colloid sample is less stable than the bulk powder sample, probably due to its higher surface area.

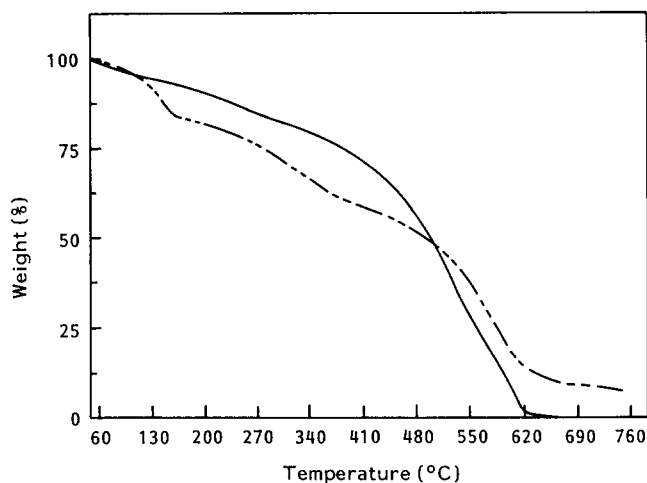


Figure 6 Thermograms of doped polyaniline colloid film (-----) and bulk polyaniline powder (————). Scan rate = $20^\circ\text{C min}^{-1}$

CONCLUSIONS

A new steric stabilizer, PVIMZ-AS, has been synthesized for the preparation of sterically stabilized polyaniline colloids. This stabilizer has a considerably higher proportion of pendant aniline groups (40 mol%) than other stabilizers previously reported.

Colloidal dispersions of polyaniline can be prepared using this stabilizer together with the KIO_3 oxidant. These dispersions have a polydisperse 'rice-grain' morphology. The more conventional $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidant cannot be used with this new stabilizer since an insoluble complex is formed. Visible absorption spectroscopy studies suggest that the PVIMZ-AS stabilizer is oxidized by the KIO_3 prior to aniline polymerization and is therefore likely to be chemically grafted to the polyaniline particles.

Scanning electron microscopy studies indicate that the colloidal polyaniline films have a fibrillar morphology and that the average fibril width is equal to that of the average rice-grain width. This suggests that end-on particle coalescence occurs during the drying process.

These colloidal polyaniline systems are more processable than bulk polyaniline films or powders. Their solid-state conductivity is lower ($10^{-2} \text{ S cm}^{-1}$) but is sufficient for cyclic voltammetry studies.

Poly(*N*-methylaniline) colloids can also be prepared using the PVIMZ-AS stabilizer and KIO_3 oxidant. Their spherical morphology suggests that the particle morphology of such sterically stabilized colloids is probably an intrinsic property of the electroactive component and is not strongly influenced by the nature of the oxidant or steric stabilizer. On the other hand, Vincent and Waterson¹⁸ have recently reported that the use of a graft/comb copolymer stabilizer with glycidyl methacrylate anchor groups can lead to the formation of spherical polyaniline particles under certain reaction conditions.

Solution-cast films made from these polyaniline dispersions exhibit poor thermal stability relative to bulk polyaniline powder due to the increased surface area of the colloidal particles.

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