Potassium iodate oxidation route to polyaniline: an optimization study

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A study of the bulk polymerization of aniline by potassium iodate in aqueous acidic media is reported. The effect of varying the solution acidity, reaction time and both the relative and absolute reactant concentrations on the polymer yield, chemical composition and compressed pellet conductivity of the polyaniline product was investigated. It is shown that substantial amounts of iodine are incorporated into the polymer, particularly at higher initial oxidant/monomer mole ratios. The chemical nature of the incorporated iodine species is complex but preliminary X-ray photoelectron spectroscopy studies suggest that several species are probably present. Partial removal of this iodine can be achieved by dedoping the polyaniline powders, indicating that at least some of the iodine is present as a dopant anion. The polyaniline powders were also characterized by scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis, and Raman spectroscopy.

(Keywords: synthesis; polyaniline; doping)

INTRODUCTION

Polyaniline is generally recognized to be the only air-stable conducting polymer[1,2]. However, commercial applications of polyaniline have not yet been successful due to the material's inherent intractability, i.e. it decomposes without melting when heated and has very low solubility in the doped, conducting state even in highly polar solvents such as dimethyl formamide or dimethyl siloxane.

Our current research programme is directed towards the preparation and characterization of novel colloidal forms of conducting polymers, such as polyaniline, in order to improve their processability[3–6]. In the course of this work it has been necessary to investigate the optimum reaction conditions for the chemical synthesis of bulk polyaniline powder.

In a previous publication[7] the use of $(NH_4)_2S_2O_8$ as an oxidant in the polymerization of aniline was reported. Recently, Pron *et al.*[8] have compared the use of four different oxidizing agents ($(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, H_2O_2 and KIO_3) in the polymerization of aniline. It was concluded that potassium iodate (KIO_3) was the most convenient oxidant, in that it produced good quality (high conductivity) polymer over a wide range of reaction conditions. We have found that this reagent is particularly useful in the synthesis of colloidal polyaniline[3,5,6].

In the present work we have extensively investigated the bulk polymerization of aniline by KIO_3 in aqueous acidic media and attempted to correlate the yield, chemical composition and solid-state conductivity of the polyaniline product with the solution acidity, reaction time and both the relative and absolute reactant concentrations.

EXPERIMENTAL

Effect of varying the relative initial reactant concentration

Aniline (1.00 ml) (vacuum-distilled and stored under argon at −29°C in the absence of light prior to use) was added in turn to seven bottles each containing 100 ml of 1.25 M HCl and varying concentrations of KIO_3 (Aldrich, used as received). These solutions were stirred at room temperature (25°C) for at least 67 h and then filtered under vacuum. In one series of experiments the resulting dark green polyaniline powders were washed first with deionized water and then with 1.25 M HCl. In a second series of experiments the powders were not subjected to any washing treatment. In both sets of experiments the powders were dried under dynamic vacuum (13.33×10^{-2} Pa) at room temperature for at least 16 h prior to weighing.

Effect of varying the reaction time on extent of polymerization

Aniline (1.00 ml) was added in turn to ten 100 ml solutions of 1.25 M HCl containing 0.90 g KIO_3. Each solution was stirred at room temperature for the desired time period (15 min–24 h), vacuum-filtered without washing, and dried under dynamic vacuum as outlined above.

Effect of varying the acidity of the reaction solution

Aniline (1.00 ml) was added in turn to seven solutions containing 0.90 g KIO_3 dissolved in 100 ml HCl of varying acidity (0.1–4.0 $mol\,l^{-1}$). The solutions were stirred at room temperature for 24 h followed by vacuum-filtration (without washing) and vacuum-drying as outlined above.

Effect of varying the absolute initial reactant concentration

A known volume of aniline (0.25–5.00 ml) was added

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in turn to six 100 ml solutions of 1.25 M HCl containing varying concentrations of KIO_3. In each reaction the initial oxidant/monomer mole ratio (*r*) was fixed at 0.38. The solutions were stirred at room temperature for 70 h, vacuum-filtered without washing and dried overnight under dynamic vacuum as outlined above.

Effect of undoping/redoping bulk polyaniline powder with NaOH and HCl solutions

Bulk polyaniline powder (~300 mg), synthesized under the conditions described in the previous paragraph, was stirred as a slurry in 100 ml 1.0 M NaOH for 3 h at room temperature. The resulting blue, undoped polyaniline powder was vacuum-filtered (yellow/brown filtrate), washed with water and then stirred as a slurry in 100 ml 1.25 M HCl for 1 h at room temperature. The final green, redoped polyaniline powder was vacuum-filtered, washed with 1.25 M HCl and dried under vacuum overnight as outlined above.

Characterization of polyaniline bulk powders

The microanalytical data for all samples were determined by Galbraith Laboratories (Knoxville, TN, USA). Compressed pellet conductivities were measured by the standard four-point probe method. The bulk powders were examined by scanning electron microscopy (SEM) (Camscan II instrument). Thermogravimetric analyses (t.g.a.) and differential scanning calorimetry (d.s.c.) measurements were made using Perkin-Elmer instruments. Preliminary X-ray photoelectron and Raman spectroscopy studies were made on the compressed pellets resulting from the conductivity measurements.

RESULTS

Figures 1–4 and *Tables 1–4* illustrate the effect of varying the solution acidity, reaction time and both the relative and absolute reactant concentrations on the polymer yield, compressed pellet conductivity and chemical composition of bulk polyaniline powder synthesized using KIO_3 as an oxidant in aqueous acidic media. Some of the polyaniline powders are believed to have become contaminated with insoluble residues from both the KIO_3 oxidant and the filter papers used for filtration. This would explain the origin of the small, variable ash content of 1–2% indicated by the microanalyses.

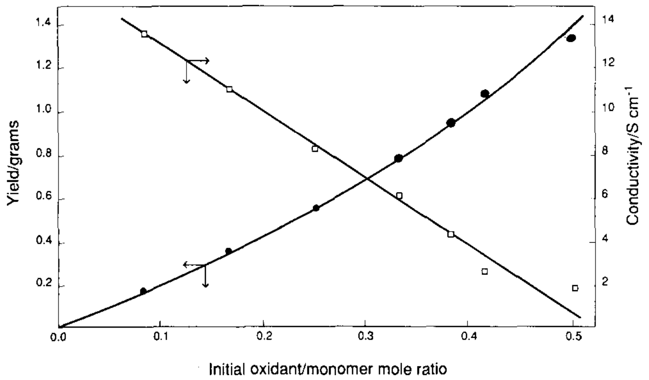

Figure 1 Effect of varying the relative initial reactant concentration on the polymer yield and conductivity. Experimental conditions: 1.0 ml aniline in 100 ml 1.25 M HCl with varying KIO_3 concentration; stirred for 67 h at 25°C

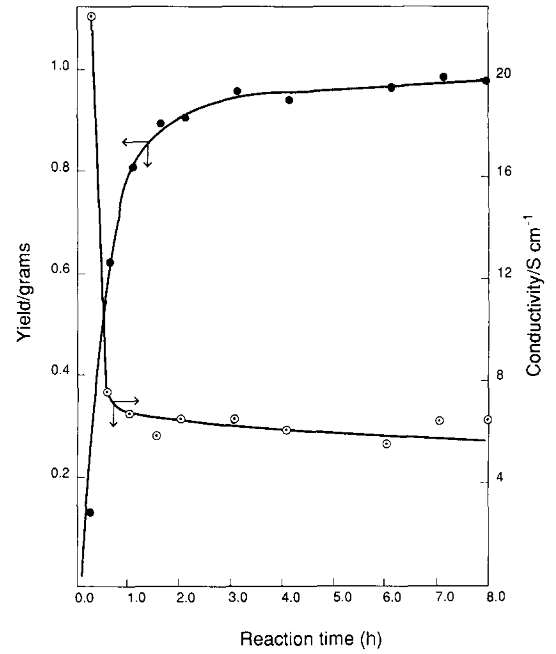

Figure 2 Effect of varying the reaction time on the polymer yield and conductivity. Experimental conditions: 1.0 ml aniline in 100 ml 1.25 M HCl containing 0.90 g KIO_3 at 25°C

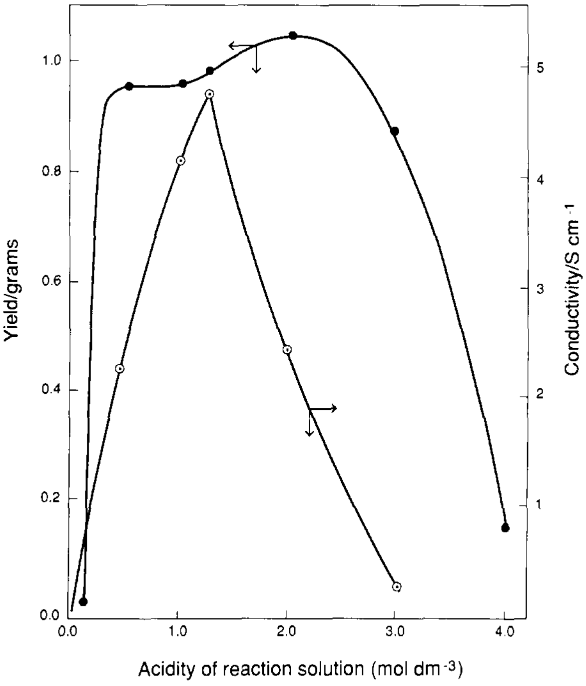

Figure 3 Effect of varying the acidity of the reaction solution on the polymer yield and conductivity. Experimental conditions: 1.0 ml aniline in 100 ml HCl (acid concentration 0.1–4.0 mol l^{-1}) containing 0.90 g KIO_3

Table 5 shows the combined effect of successive base (NaOH) and acid (HCl) treatments on the chemical composition and compressed pellet conductivity of bulk polyaniline powder synthesized using KIO_3 (*Table 4*, sample 3).

Thermogravimetric analyses of the doped, conducting polyaniline prepared with both KIO_3 and $(NH_4)_2S_2O_8$ oxidants were measured in air at a scan rate of 20°C min^{-1}. No significant differences were observed between the two samples.

SEM studies indicated that the KIO_3-synthesized bulk polyaniline powder (*Table 3*, sample 4) has a 'rice-grain' morphology with grain lengths in the range 0.5–1.0 μm and grain widths in the range 0.1–0.2 μm (ref. 6).

D.s.c. studies (in a nitrogen atmosphere, scan rate 20°C min^{-1}) revealed a broad peak centred at 95–120°C. After cooling the sample under nitrogen and repeating the d.s.c. scan this peak disappeared.

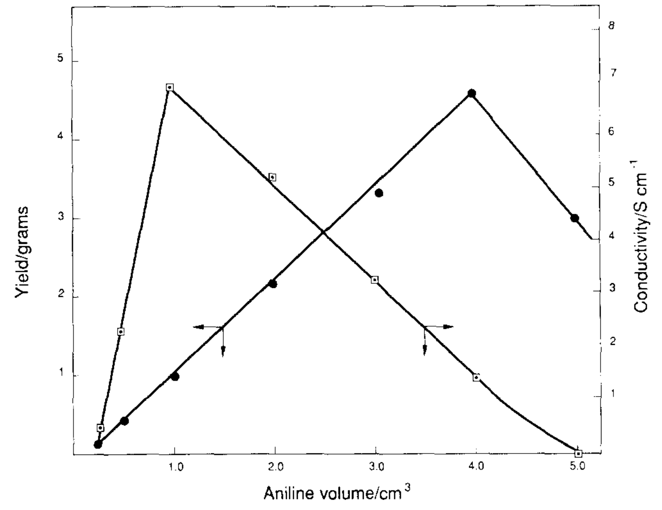

Figure 4 Effect of varying the absolute initial reactant concentration on the polymer yield and conductivity. Experimental conditions: 0.25–5.0 ml aniline in 100 ml 1.25 M HCl containing 0.22–4.51 g KIO_3 at 25°C. The initial oxidant/monomer mole ratio was held constant at 0.38

DISCUSSION

In a previous paper[7] the polymerization of aniline using $(NH_4)_2S_2O_8$ as an oxidant was investigated. It was shown that higher polymer yields were obtained by increasing the initial oxidant/monomer mole ratio (r) up to $r \approx 1.0$. Assuming the persulphate anion was acting as a two-electron acceptor:

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad (1)$$

Overall the results suggested that, on average, ~2.3 electrons were removed from each aniline monomer unit. For values of $r > 1.5$ the polymer yield was reduced, presumably due to over-oxidation of the polyaniline chains with concomitant formation of soluble side-products. This interpretation was supported by conductivity measurements made on compressed pellets of bulk polyaniline powders: constant conductivities (18 ± 2 S cm^{-1}) were obtained for $0.25 < r < 1.25$, with a monotonic decrease in conductivity for $r \geqslant 1.25$.

Recently Pron *et al.*[8] have reported that KIO_3 in aqueous HCl can be used to prepare 'good quality samples' of polyaniline at 0°C. These workers claimed that the IO_3^- anion was acting as a six-electron acceptor according to:

$$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O \qquad (2)$$

No mention was made of the alternative half-reaction in which the IO_3^- anion acts as a five-electron acceptor, even though the redox potentials for these two half-reactions are almost indistinguishable[9]:

$$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O \qquad (3)$$

It was further shown on the basis of microanalytical

Table 1 Effect of varying the relative initial reactant concentration on the chemical composition of the polyaniline powders. Experimental conditions: 1.0 ml aniline in 100 ml 1.25 M HCl with varying KIO_3 concentration, stirred for 67 h at 25°C

Sample no.	Initial oxidant/ monomer mole ratio	Microanalytical data (%) C	H	N	I	Cl	O	Σ
1	0.08	55.81	4.80	10.57	4.46	13.72	9.73	99.09
2	0.17	53.46	4.85	10.00	8.62	12.06	9.70	98.69
3	0.25	50.51	4.38	9.33	13.35	11.60	9.13	98.30
4	0.33	47.88	4.13	8.76	18.29	10.93	8.34	98.33
5	0.38	47.03	3.86	8.44	20.68	10.59	8.27	98.87
6	0.42	45.71	3.73	8.28	23.89	9.82	6.93	98.36
7	0.50	42.68	3.47	7.54	28.84	9.66	6.64	98.83

Table 2 Effect of varying the reaction time on the chemical composition of the polyaniline powders. Experimental conditions: 1.0 ml aniline in 100 ml 1.25 M HCl containing 0.90 g KIO_3 at 25°C

Sample no.	Reaction time (h)	Microanalytical data (%) C	H	N	I	Cl	O	Σ
1	0.25	51.94	5.31	10.30	4.80	14.01	12.05	98.4
2	0.55	46.86	4.67	9.17	12.51	14.72	10.20	98.1
3	1.00	45.38	4.07	8.50	19.40	12.36	7.89	97.7
4	2.00	45.11	3.88	8.19	21.64	11.62	7.93	98.4
5	4.00	45.16	3.92	8.21	21.74	11.34	7.71	98.1
6	8.00	45.30	3.88	8.18	21.65	11.07	7.87	98.0
7	24.00	45.31	3.87	8.14	21.65	10.72	7.87	97.5

Table 3 Effect of varying the acidity of the reaction solution on the chemical composition of the polyaniline powders. Experimental conditions: 1.0 ml aniline in 100 ml HCl (acid concentration 0.1–4.0 mol l^{-1}) containing 0.90 g KIO_3

Sample no.	Acid concentration (mol dm^{-3})	Microanalytical data (%) C	H	N	I	Cl	O	Σ
1	0.10	[a]	[a]	[a]	[a]	[a]	[a]	
2	0.50	44.93	3.68	8.28	24.81	9.42	6.96	98.1
3	1.00	45.53	3.98	8.36	22.69	11.69	7.46	99.7
4	1.25	45.01	3.99	8.13	23.74	12.41	7.58	100.9
5	2.00	42.47	3.36	7.38	31.67	7.53	5.38	97.8
6	3.00	40.00	3.01	6.84	34.35	8.05	5.82	98.0
7	4.00	39.53	2.10	5.56	24.54	21.59	5.46	98.7

[a] Insufficient yield for microanalysis

Table 4 Effect of varying the absolute initial reactant concentration on the chemical composition of the polyaniline powders. Experimental conditions: 0.25–5.0 ml aniline in 100 ml 1.25 M HCl containing 0.22–4.51 g KIO_3 at 25°C. The initial oxidant/monomer mole ratio was held constant at 0.38

Sample no.	Aniline concentration (v/v%)	Microanalytical data (%) C	H	N	I	Cl	O	Σ
1	0.25	43.46	2.83	6.18	[a]	[a]	7.94	–
2	0.50	44.40	3.38	6.97	28.36	7.04	7.76	97.9
3	1.00	45.13	3.78	8.01	23.52	9.50	7.83	97.8
4	2.00	45.99	4.01	8.49	20.78	11.59	7.42	98.3
5	3.00	46.79	4.54	6.93	20.20	12.57	7.87	98.9
6	4.00	43.12	3.57	8.08	27.29	10.72	6.39	99.2
7	5.00	27.94	2.85	5.34	47.19	0.78	14.04	98.1

[a] Insufficient sample for microanalysis

Table 5 Effect of undoping/redoping KIO_3-synthesized polyaniline with NaOH and HCl solutions on its chemical composition and conductivity

	Microanalytical data (%) C	H	N	I	Cl	O	Σ	Conductivity (S cm^{-1})
Sample 3 (see *Table 4*)	45.13	3.78	8.01	23.52	9.50	7.83	97.8	7.0
Sample 3 after undoping/redoping	49.08	4.01	8.61	18.15	11.43	7.86	99.1	1.4

data that the iodine content of the polyaniline powders was negligible (below the detection limit of 0.3%), at least for an initial KIO_3/aniline mole ratio of 0.065.

The present work is concerned with the polymerization of aniline at 25°C using KIO_3 as an oxidant over a wide range of experimental conditions. The original aim was to optimize the reaction conditions so as to obtain polyaniline in good yield (~ 1 g polymer per gram of monomer) and of reasonable conductivity ($\geqslant 1$ S cm^{-1}). We have recently reported that these optimized reaction conditions are suitable for the preparation of colloidal dispersions of polyaniline and that such systems significantly improve the processability of the normally intractable conducting polymer component[3–6].

Effect of varying the relative initial reactant concentration

All the data shown in *Figure 1* and *Table 1* are for the unwashed polyanilines (see Experimental section). No significant differences were observed between washed and unwashed samples. The polymer yield increased monotonically with increasing initial oxidant/monomer mole ratio *r* (see *Figure 1*). However, the compressed pellet conductivity of the bulk powders decreased with *r*. The microanalytical data presented in *Table 1* clearly indicate that, in contrast to the work of Pron *et al.*[8] significant quantities of iodine are incorporated into the polyaniline powders as *r* is increased. If this is chemically bound as some form of dopant anion (I^-, I_3^-, I_5^- etc.), or even covalently bonded to the polyaniline chains, then it would be incorporated at the expense of atoms lighter than itself (C, H, N, O or Cl). Alternatively the iodine could be merely physically absorbed as I_2. In either case the effective yield (mass) of polyaniline would be increased. The presence of iodine in the polyaniline bulk powder is not particularly desirable since it results in reduced conductivity and could also render the material unsuitable for certain speciality applications (e.g. anti-corrosion coatings). Bearing in mind the previously stated criteria regarding yield and conductivity, a value of $r = 0.38$ was taken to be a reasonable compromise for our conflicting requirements. This value of r was used in all of the remaining experiments.

Effect of varying the reaction time on the extent of polymerization

The polymer yield became constant within 6 h at 25°C, indicating the end of the polymerization (see *Figure 2*). For reaction times longer than 1 h the conductivity of the bulk powder was constant within experimental error, but for shorter reaction times the conductivity was somewhat higher. This appears to be related to the marked increase in iodine content in the polyaniline powders as the polymerization proceeds (see *Table 2*). Clearly the iodine originates from the KIO_3 oxidant which reacts according to either equation (2) or equation (3) or some combination of the two processes. Regardless of the actual mechanism, at short reaction times most of the IO_3^- anion remains unreacted and therefore the concentration of iodine species in the reaction solution is relatively low. Thus less iodine is available to be absorbed by the polyaniline powder. As the polymerization proceeds the IO_3^- anion is reduced and iodine species are generated which become incorporated into the polyaniline product.

Effect of varying the acidity of the reaction solution

Good polymer yields (~ 1 g) are obtained if the HCl concentration lies in the range 0.5–2.0 M. All four samples prepared in this range had reasonable conductivities (> 1 S cm^{-1}). Lower acidity (0.1 M HCl) caused a dramatic reduction in polymer yield whilst higher acid concentrations had a deleterious effect on conductivity (3.0 M HCl) or on both conductivity and yield (4.0 M HCl). The iodine content of the polyaniline powder prepared in 2.0 M HCl was significantly higher than for samples prepared in 0.5 M, 1.0 M or 1.25 M HCl (see *Table 3*, samples 2–5). The polyaniline powder synthesized in 1.25 M HCl had the highest conductivity of all the samples and consequently this acid concentration was considered to be the most suitable.

Effect of varying the absolute initial reactant concentration

The polymer yield increases linearly with aniline concentration from 0.25 to 4.0 v/v% before decreasing sharply at 5.0 v/v% (see *Figure 4*). Microanalytical data for the latter sample suggests that the polymer obtained in this case is not polyaniline. The maximum conductivity was observed for the 1.0 v/v% sample but conductivities >1 S cm^{-1} were obtained for all samples between 0.50 v/v% and 4.0 v/v%. Although all other polyaniline syntheses in the present work were carried out at an aniline concentration of 1.0 v/v% it seems that this reactant concentration can be increased by a factor of four without seriously reducing the electroactivity of the bulk powder. This information may also prove useful in the preparation of more concentrated colloidal dispersions of polyaniline (currently the dispersions are prepared at aniline concentrations of 1.0 v/v%). Conductivity measurements on sample 7 (prepared at 5.0 v/v%) confirmed that the polymeric product was electrically insulating and therefore not polyaniline. It is unclear at present why there should be such a marked difference between the polymeric material obtained at 4.0 v/v% and that at 5.0 v/v%.

Effect of undoping/redoping bulk polyaniline powder with NaOH and HCl solutions

The microanalytical data presented in *Table 5* indicate a partial loss of iodine from the polyaniline bulk powder during the undoping/redoping treatment together with a concomitant increase in chlorine content (the C, H, N and O contents are essentially unchanged). Thus we must conclude that at least some of the iodine originally contained in the polyaniline is present as dopant anions (I^-, I_3^-, I_5^-). If we assume that all of the reduction in iodine content is due to the loss of I^- anions only, then we find that the observed increase in chlorine content is entirely consistent with the simple replacement of I^- by Cl^-. If the undoping treatment with NaOH solution is carried out for longer reaction times (18 h rather than 3 h) then no further reduction in iodine content is observed. This suggests that most of the iodine found in these polyaniline samples is present as either I_2 or is somehow covalently bound to the polymer backbone.

Nature of iodine species in polyaniline

The preliminary X-ray photoelectron spectroscopic (X.p.s.) studies on the polyaniline powders as compressed pellets are consistent with the coexistence of several iodine species in the samples. The two peaks due to I 3d 3/2 and I 3d 5/2 are broad and asymmetric and are shifted to somewhat higher energies than those observed for the polyaniline colloids[5]. In the latter system the X.p.s. spectra have peaks with rather narrower band widths. Raman spectroscopy has unambiguously confirmed the presence of the linear tri-iodide anion in both the bulk powders and the colloids[5] (presumably it is formed by the combination of iodine and iodide anion). It should be noted that the ultra-high vacuum conditions (13.33×10^{-7} to 13.3×10^{-9} Pa) required for the X.p.s. experiments would almost certainly result in at least a partial loss of physically absorbed iodine from the samples if such species were present. Such unavoidable perturbations would make the reliable quantitative assessment of the relative abundance of the various iodine species extremely difficult, if not impossible.

If the polyaniline bulk powders are washed with organic solvents such as acetone or ethanol in either the doped or undoped state the solvent turns brown, suggesting that molecular iodine is present in the material and is easily leached out.

Preliminary secondary ion mass spectroscopic studies at first sight seem to indicate the presence of a covalent carbon–iodine bond in the polyaniline powders[10]. It is known that the oxidative polymerization of aniline in acidic media proceeds via a pink-coloured anilinium radical cation intermediate[7]. If KIO_3 is used as the oxidant in this process then I_2 may be generated either from the reaction depicted in equation (3) or from the reaction of excess IO_3^- with I^- (ref. 11):

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 6H_2O \qquad (4)$$

It is unlikely that iodine is capable of iodinating aniline monomer or, indeed, the polyaniline chain directly. However, it is not inconceivable that iodine could iodinate the rather more reactive anilinium radical cation prior to its incorporation into the polyaniline backbone.

It would appear that the chemical nature of the iodine species in the polyaniline samples is indeed complex, with I_2, I^-, I_3^- and probably covalently bound iodine all present, albeit in unknown proportions.

Other characterization methods

SEM studies on the bulk polyaniline powders reveal a globular 'rice grain' morphology similar to that previously reported for the polyaniline colloids[3,5,6]. However, the bulk powder rice grain features are fused together rather than being discrete particles, and their average dimensions are up to 10 times larger. These results suggest that the observed colloid morphology may be an intrinsic property of the polyaniline component rather than being merely due to the colloid synthesis conditions.

The d.s.c. experiments strongly suggest that the polyaniline powders contain absorbed water which is probably associated with the dopant anions[8]. This accounts at least qualitatively for the variable oxygen content (5–14%) found in all the samples.

The long term stability of the compressed pellet conductivity of the polyaniline samples was excellent with no measurable loss in performance over a period of more than 1 year.

CONCLUSIONS

The bulk polymerization of aniline by KIO_3 in aqueous acidic media has been extensively investigated. The effect of varying the solution acidity, reaction time and both the relative and absolute reactant concentrations on the polymer yield, chemical composition and conductivity of the polyaniline powders has been optimized.

Unlike Pron *et al.*[8], whose studies were admittedly carried out at different temperature (0°C), absolute and relative reactant concentrations (4.15 v/v% and $r = 0.065$ respectively), and solution acidity (2.0 M HCl), we find that substantial quantities of iodine are incorporated into the polyaniline powders.

The X.p.s. studies indicate that several iodine species coexist in the polyaniline powders. Raman spectroscopy has confirmed the presence of I_3^- whilst undoping/redoping experiments are best explained by assuming the iodine dopant anion is I^-. Molecular iodine can easily be leached out of the powders by treatment with various organic solvents. Preliminary SIMS studies suggest that some of the iodine is chemically bound to the polyaniline backbone.

On the basis of the above evidence it seems unreasonable to represent the reduction of the iodate anion simply by equation (2) as proposed by Pron *et al.*[8]. Equations (3) and/or (4) are also important and so the number of electrons accepted per iodate anion probably lies somewhere between five and six.

Our optimized reaction conditions for the polymerization of aniline by KIO_3 in HCl are as follows: 1.0 ml aniline is added to 0.90 g KIO_3 dissolved in 100 ml 1.25 M HCl at 25°C and allowed to react for at least 6 h. These conditions were used in a slightly modified form (addition of a tailor-made polymeric surfactant at 1.0 w/v% concentration) for the preparation of polyaniline colloids[3,5,6]. It seems that for the preparation of bulk powders, the absolute concentration of the reactants could be increased up to four-fold (see Discussion section) without significant losses in yield or conductivity. However, this may not necessarily prove desirable for the polyaniline colloids since the increased rate of polymerization could lead to destabilization and precipitation of the sterically-stabilized polyaniline particles.

SEM studies confirm that the rice grain morphology of the polyaniline bulk powders is similar to that previously reported for the polyaniline colloids[3,5,6]. This suggests that the morphology of the colloidal particles is due to some intrinsic property of polyaniline and probably cannot be significantly altered by modifying the colloid synthesis conditions.

The polyaniline bulk powders contain adsorbed H_2O which is probably associated with the dopant anions (Cl^-, I^-, I_3^-). The thermal stability of polyaniline is not improved by the use of KIO_3 oxidant instead of $(NH_4)_2S_2O_8$. The room temperature air-stability of the conductivity of the bulk powder is excellent for both oxidants.

The high iodine content of polyaniline synthesized using the KIO_3 oxidant is undesirable and could prevent the material finding use in several application areas (e.g. anti-corrosion coatings). Accordingly our future work will be concerned with the reduction or preferably elimination of the iodine species in both polyaniline bulk powders and colloids.

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