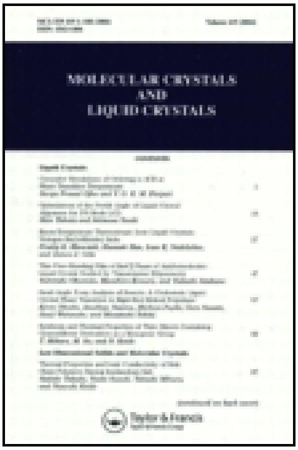

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Synthesis and Characterization of Aqueous Colloidal Dispersions of Poly(Vinyl Alcohol)/Polyaniline Particles

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Colloidal polyaniline has been prepared in acidic aqueous media by a modified chemical polymerization of aniline in the presence of a tailor-made polymeric surfactant. The surfactant which acts as a steric stabilizer used in this study is derivatized poly(vinyl alcohol-co-vinyl acetate). This surfactant 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 novel 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 surprisingly high (≃1 S/cm), despite the presence of the insulating outer layer of chemically-grafted stabilizer. We have characterized these polyaniline colloids by a wide range of techniques including electron microscopy, cyclic voltammetry and Raman, visible absorption and X-ray photoelectron spectroscopy.

INTRODUCTION

Since the "*rediscovery*" of polyaniline as a conducting polymer few years ago,[1-4] a wealth of information has been obtained on the material's synthesis and properties. The polymer is typically prepared by oxidation of aniline monomer in aqueous acidic media using reagents such as ammonium persulfate or potassium dichromate.[5,6] A non-oxidative proton-doping process results in a highly environmentally stable material with a room temperature conductivity in the range 1–10 S/cm. Although its air-stability is attractive, polyaniline suffers from poor processability, being only slightly soluble in polar solvents such as dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO).[7] However, a good solubility is achieved in strong acidic media such as concentrated sulfuric acid.[8]

Intractability is typical of conjugated polymers because of the aggregated character associated with strong interchain interactions. To take advantage of this property the preparation of conducting polymers as colloidal dispersions seemed

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to be an excellent approach toward processability. Since 1986 several groups have described the preparation of spherical sub-micronic polypyrrole colloidal particles in aqueous media.[9-14] The particles are sterically-stabilized by an outer layer of physically adsorbed polymeric surfactant such as methylcellulose, poly(vinyl alcohol-co-vinyl acetate), poly(vinyl pyrrolidone), poly(vinyl pyridine-co-butyl methacrylate), etc. Most of our initial attempts to produce colloidal polyaniline particles by analogous methods have resulted in macroscopic precipitation due to inefficient adsorption of the stabilizer, although in certain cases a low yield of colloidal polyaniline has been reported.[15,16] To achieve colloidal stability of polyaniline particles and avoid the problems associated with physical adsorption/desorption, we employed another synthetic approach which consisted of graft copolymerization of aniline onto the appropriate polymeric surfactant. In a recent preliminary communication[17] we described the preparation of colloidal polyaniline particles using a tailor-made random copolymer poly(2-vinyl pyridine-co-*p*-aminostyrene) as a polymeric surfactant. Preparation of the latter and evidence of grafting were described recently.[18] A detailed account of the synthesis and properties of the colloidal particles will be published elsewhere.[19]

In this paper, we describe the preparation and characterization of polyaniline colloids using the derivatized poly(vinyl alcohol-co-vinyl acetate) as a steric stabilizer in the graft copolymerization process.

EXPERIMENTAL

Preparation of the Steric Stabilizer

Commercially available poly(vinyl alcohol-co-vinyl acetate), PVA, whose nominal molecular weight is 25,000 or 125,000 was dissolved with stirring at 130°C in DMF under argon. Triethylamine and a DMF solution of *p*-nitrobenzoyl chloride (1–6 mol% relative to the PVA base monomer) were added in turn to the reaction solution and esterification allowed to proceed for 16–24 hrs. An 8–10 mole excess of phenylhydrazine (based on *p*-nitrobenzoyl chloride) was then added to the reaction solution and its temperature was raised to reflux for 16–24 hrs. The reaction product was purified by repeated precipitation from water/acetone or water/THF solvent/non-solvent mixtures. The reaction scheme is shown in Figure 1.

Preparation of Polyaniline Colloids

The synthesis which utilized potassium iodate to oxidize aniline was carried out as follows: potassium iodate (0.90 g) and stabilizer (0.4–1.0 g) were dissolved together in 100 ml of 1.25 M hydrochloric acid at room temperature. The solution was allowed to age for 0 to 30 min. to insure a maximum yield of the oxidation reaction of the *p*-aminostyrene moiety in the copolymer. Aniline (1.0 ml) was injected into the stirred reaction mixture and allowed to react for 2 days. At the end of this period the reaction medium turned dark green. The dispersion was centrifuged at 18,000 rpm for 2 hrs, the supernatant decanted, and the dark green sediment redispersed in 1.25 M HCl *via* ultrasonics.

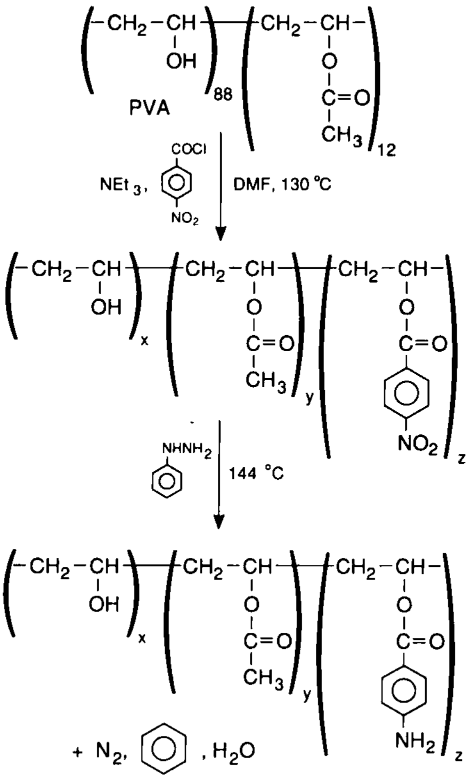


FIGURE 1 Synthesis of polyaniline stabilizers by chemical modification of poly(vinyl alcohol-co-vinyl acetate).

Characterization of Stabilizer and Colloids

The graft copolymer steric stabilizer was characterized by gel permeation chromatography (GPC), and NMR to determine molecular weights, distribution and co-monomer ratios in the resulting material. Polyaniline colloids were characterized using a wide range of techniques including transmission, scanning and scanning tunneling microscopies, cyclic voltammetry and Raman, uv-visible absorption and X-ray photoelectron spectroscopies. Conductivity measurements as a function of temperature and pressure were performed on films cast from the colloidal dispersions.

RESULTS AND DISCUSSION

Oxidant/Stabilizer Compatibility

The oxidation/polymerization of aniline in the presence of the derivatized PVA stabilizer was attempted using several oxidants that are typically used for the synthesis of bulk polyaniline. It was expected that the pendant aniline moiety in the graft copolymer would participate in the polymerization of aniline *via* a mechanism similar to that outlined previously.[7] Recently, Pron *et al.*[20] reported that potassium iodate could be used over a wide range of reaction conditions to produce good quality bulk polyaniline powder. We found that this oxidant did not cause precipitation of the stabilizer; as a consequence it became the reagent of choice for the preparation of colloidal polyaniline.

Molecular Weight and Composition of the Stabilizer

Gel permeation chromatographs of the underivatized commercial PVA and the chemically modified version indicated significant chain scission occurred as a result of the grafting process of *p*-aminostyrene, probably during the reduction of the nitro groups. This degradation is undesirable because in some cases the derivatized PVA did not produce stable colloidal dispersions of polyaniline, particularly when PVA whose nominal manufacturer's molecular weight is 25,000 was used as the starting material. This is presumably due, at least in part, to it's lowered molecular weight. The results are summarized in Table I.

In principle there are several ways to minimize or even prevent the polymer chain scission. For example, the use of a milder reducing agent than phenylhydrazine such as $TiCl_3$ could prove beneficial.[21] Alternatively, the reduction step could be eliminated if primary aromatic groups were introduced directly. This could be achieved either by trans-esterification of the PVA[22] using methyl *p*-aminobenzoate or by using reagents such as *p*-aminosalicyloyl chloride instead of *p*-nitrobenzoyl chloride in the esterification reaction.[23]

We have determined the mol% of grafted pendant aniline groups onto PVA by means of ^1H NMR. Both PVA starting materials consisted of 88 mol% vinyl alcohol and 12 mol% vinyl acetate. The resulting grafted amount was 1.7 mol% for PVA (25,000) and 1.8 mol% for PVA (125,000).

Spectroscopic Evidence for Grafting of Polyaniline

The polymerization of aniline by KIO_3 (and other oxidants such as ammonium persulfate) in acid solutions proceeds *via* a short-lived anilinium radical cation

TABLE I

Effect of derivatization on the molecular weight* of PVA

Starting Material		M_w	M_w/M_n
PVA (25,000)**	before grafting	31,900	2.3
	after grafting	22,700	2.3
PVA (125,000)**	before grafting	101,800	1.9
	after grafting	40,200	2.4

*As measured by gel permeation chromatography
**Nominal manufacturer's molecular weight

intermediate which has an absorption peak λ_{max} at 525 nm (Figure 2). If KIO_3 is added to an acidic solution containing the polymeric stabilizer, a similar absorption peak is observed. In a control experiment, an underivatized poly(vinyl alcohol-co-vinyl acetate)/KIO_3/HCl solution showed no absorption peak under identical conditions. Thus, we conclude that the observed absorption peak is due to the oxidation of the pendant aniline groups. An absorption spectrum of colloidal polyaniline is shown in Figure 2 for comparison. The latter spectrum is identical to that reported for electrochemically-synthesized polyaniline film.[24] In our preparative procedure for the synthesis of colloidal polyaniline, the aniline monomer is added last to a stirred solution containing KIO_3 and the stabilizer. Since it is clear that the pendant aniline groups grafted onto PVA are activated under these conditions, we believe that these moieties inevitably participate in the aniline polymerization and constitute sites for the grafting of polyaniline onto the stabilizer's chain. The strong interchain interaction in polyaniline sequences leads to chain association and formation of particles with colloidal stability provided by the polymeric surfactant.

Colloids Morphology

Examination of the dried-down dispersions by scanning and transmission electron microscopies revealed a morphology which consisted of "*rice grain*" like particles. The length of the particles was 150 ± 50 nm and their width was 60 ± 10 nm. Figure 3 shows scanning electron micrographs of bulk polyaniline prepared using potassium iodate and of the colloidal dispersions for comparison (Figures 3a and

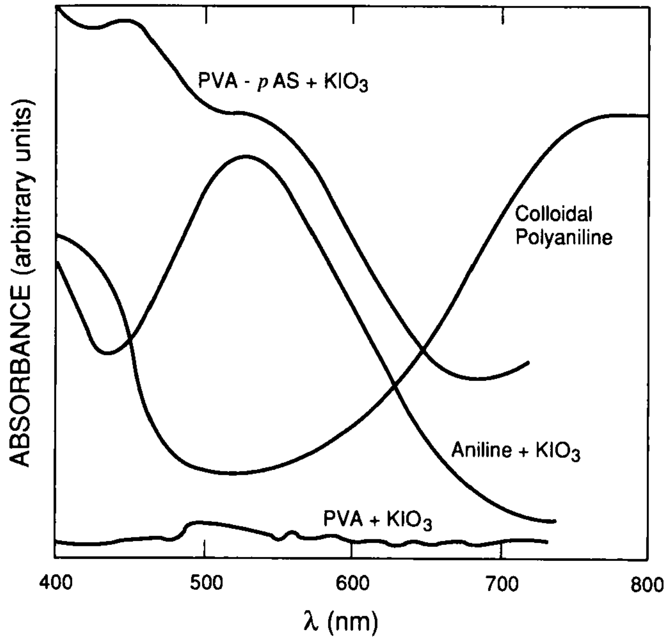


FIGURE 2 Spectroscopic evidence for grafting of polyaniline.

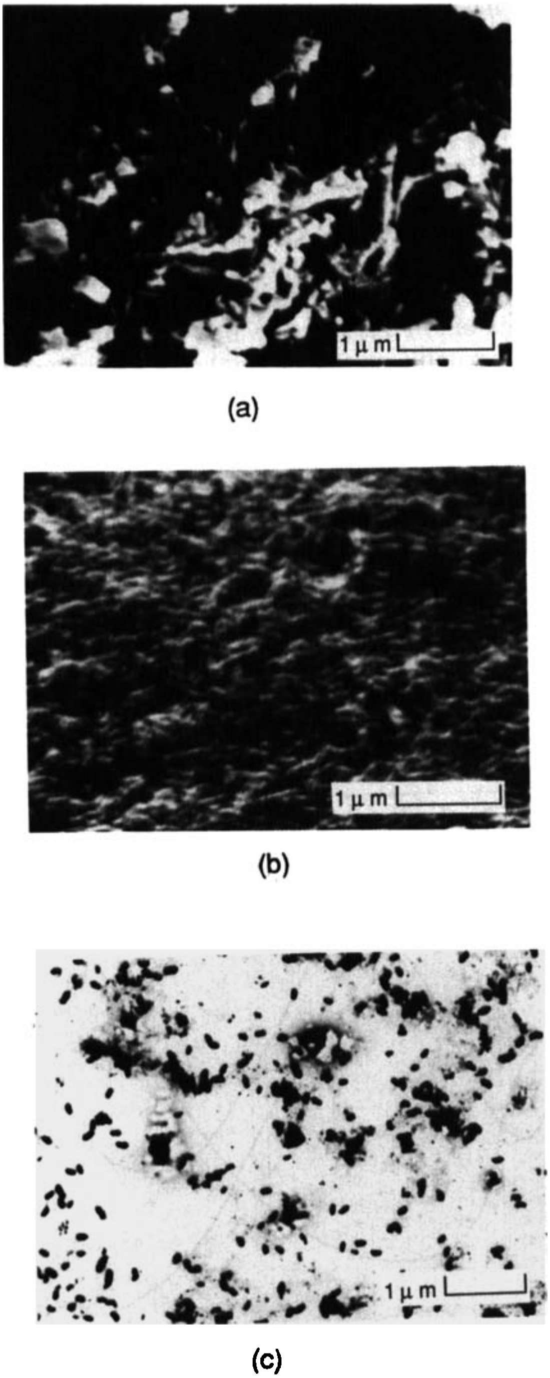


FIGURE 3 Scanning electron micrographs of bulk polyaniline (a) and colloidal polyaniline (b); and transmission electron micrograph of (b).

3b). Figure 3c shows a transmission electron micrograph of the dispersions in which individual particles can be seen clearly. From these results, it is clear that bulk polyaniline particles aggregate in the form of much larger particles (fibrils) than what is observed for the colloidal dispersions. Because steric stabilization by the polymeric surfactant takes place during polymerization of aniline, aggregation is limited to aggregates or particles in the sub-micronic range. However, the overall fibrillar shape is maintained. Although, the shape of the particles is non spherical (unlike polypyrrole), scanning tunneling microscopy revealed that any given polyaniline colloidal particle is composed of much smaller ones whose shape is undetermined. The morphology using this latter technique will be discussed elsewhere.[25]

Conductivity

Four-probe conductivity measurements were performed on films cast from the dark green dispersions. Room temperature conductivity varied from sample to sample and was in the range 0.5–2.0 S/cm. This conductivity is comparable to that of bulk polyaniline prepared chemically or electrochemically despite the presence of the non-conducting component which is the PVA-based polymeric surfactant. Scanning tunneling microscopy[25] indicated the absence of surfactant chains where there is contact between the conducting components once the solvent is removed. This allows for the hopping of charge carriers between the colloidal particles. Conductivity measurements as a function of pressure and temperature[25] indicated that conduction is pressure-dependent and occurs *via* a variable-range hopping mechanism.

Cyclic Voltammetry

Cyclic voltammograms (CV's) for a latex film on a platinum disk electrode are given in Figure 4a for scan rates in the range 10–100 mV/sec. The film was formed by placing a drop of the colloidal dispersion on the electrode surface and allowing the solvent to evaporate. The CV's in Figure 4a were taken in a limited potential range to avoid over-oxidation of the polymer. This data is similar to that obtained for anodically grown bulk polyaniline films on platinum electrodes with no indication of significant effects of the surfactant layer. The variations in reversibility with scan rate indicate a limited rate of electrochemical charging, probably, due to the limited concentration and/or conductivity of the electrolyte. The latex film is rather thick, with a charge capacity of the order of 250 mC/cm^2, and the RC time constant determined by the ohmic resistance of the electrolyte. The film capacity may thus be of the order of 0.1–1.0 sec. Another factor in the electrochemical response could be the limited concentration of chloride ions, as can be realized from electrolyte composition effects on the apparent reversibility of charging shown in Figure 4b. Figure 4c shows that, following cycling with higher anodic end potentials, another more anodic redox systems of lower reversibility becomes apparent. Such increase of the anodic end potential causes also a lowering of the charge capacity in the region of the first anodic peak and the emergence of a third

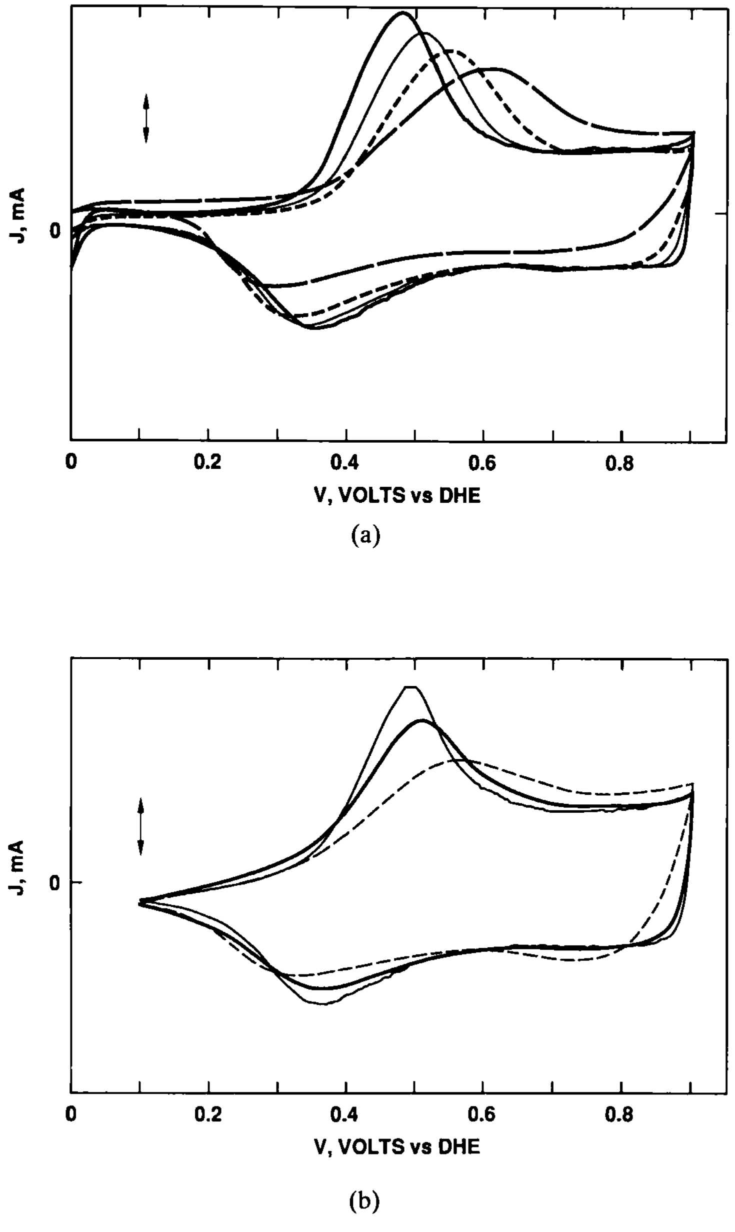
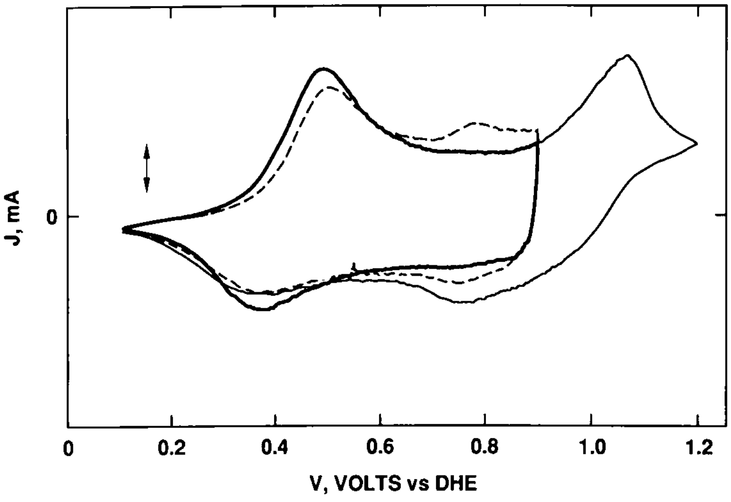


FIGURE 4 (a) Cyclic voltammograms of a colloidal polyaniline film recorded in 2M HCl solutions at scan rates of 10 mV/sec (thick solid curve), 25 mV/sec (solid thin curve), 50 mV/sec (short-dashed curve) and 100 mV/sec (long-dashed curve). The current bar corresponds to 4, 10, 20 and 40 mA/cm^2 respectively. (b) Cyclic voltammograms for a colloidal polyaniline film recorded in 0.2 M HCl (dashed curve), 0.2 M HCl, KCl (thick solid curve) and 2M HCl (thin solid curve). The scan rate is 10 mV/sec and the current bar corresponds to 4 mA/cm^2 in each case. (c) Cyclic voltammograms of a colloidal polyaniline film recorded in 2M HCl solutions in a restricted potential domain (thick solid curve), in an extended potential domain (thin solid curve) and returning subsequently to the restricted domain (dashed curve). Scan rate is 10 mV/sec and current bar corresponds to 4 mA/cm^2.



(c)

FIGURE 4 (*continued*)

intermediate pair of voltammetric peaks. This pattern is known for anodic bulk polyaniline films, and is associated with over-oxidation of the polymer.

These preliminary results show charging characteristics very similar to those of anodically formed polyaniline films. More detailed impedance measurements are required to determine any intrinsic charging barriers in the latex films caused by the presence of thin layers around the conducting polymer cores.

Stability of Polyaniline Colloids

We have observed that the colloidal stability of polyaniline/PVA dispersions is not as good as that of the previously reported polyaniline/poly(vinyl pyridine) systems.[17] In fact, precipitation starts to occur after a few weeks upon standing. This suggests that derivatized PVA is less efficient as a steric stabilizer than poly(vinyl pyridine-co-*p*-aminostyrene). Furthermore, the chain scission which occurs during the derivatization process and results in lower molecular weights than that of the starting PVA material might cause the relative colloidal instability. A better stability of the dispersions with PVA (125,000) than that of the dispersions with PVA (25,000) supports the above assumption.

Air-stability of polyaniline colloids is usually excellent and similar to that of bulk polyaniline. When monitored over several months, room temperature conductivity remains constant. Furthermore, the insulating outer layer constitutes an oxygen barrier which should enhance air-stability. This feature, combined with processability makes polyaniline colloids attractive materials for technological applications.

Thermogravimetric analysis data of bulk and colloidal polyaniline in air (prepared using potassium iodate) is shown in Figure 5. Decomposition of the colloids follows a similar trend to that of the bulk polymer. For both materials, the gradual weight loss attains a value of approximately 10% at 150°C. However, the weight loss beyond this temperature is higher than for the bulk polymer. This could be due

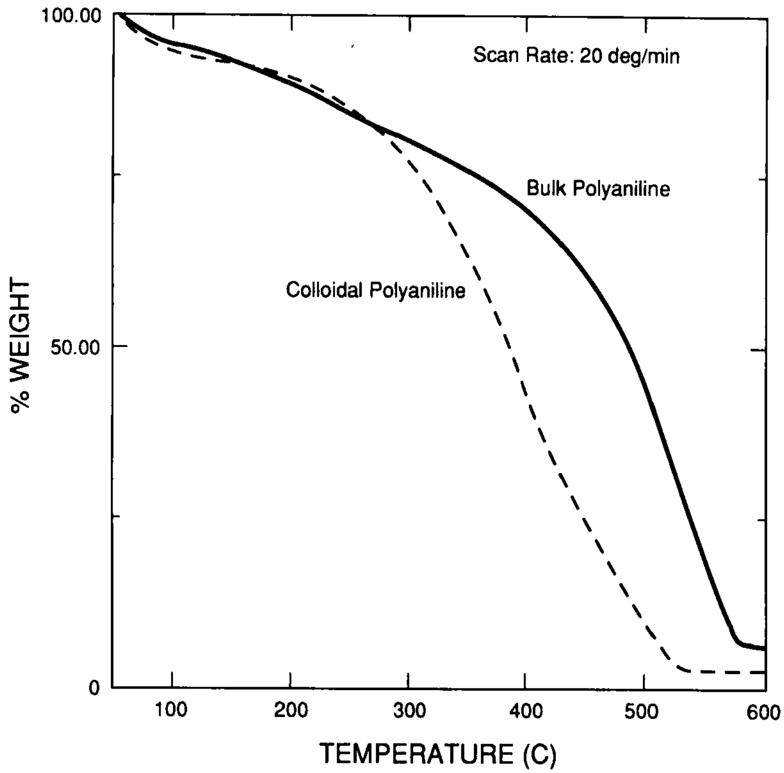


FIGURE 5 Thermogravimetric analysis of bulk and colloidal polyaniline in air.

to shorter polyaniline grafts than in the bulk form and possibly to less interchain interaction resulting from the distribution of the grafting sites. The effect of such degradation on conductivity has not been determined yet.

Structure of the Colloids

Microanalysis data on the colloids are consistent with the calculated values for each element of the copolymer backbone. What is of interest to us are the weight fractions of chlorine and iodine species that are due to the oxidation process, which results in their incorporation as counter-ions, and the iodine and chlorine to nitrogen ratios. In a specific example, the analysis gave 6.91, 7.84, and 20.28 weight% for nitrogen, chlorine and iodine respectively. Raman spectroscopy showed that iodine species were in the form of mostly I_3^- and a small amount of I_5^- (Figure 6). Displayed in the figure are spectra of the colloid as-synthesized (6b), the bulk polymer dedoped and redoped with HCl (6a) and the bulk polymer obtained by oxidation with ammonium persulfate (6c) for comparison. At a first approximation, we will consider that iodine exists in the form of triiodide ions only (Raman peak at 107 wavenumber). In this case, iodine accounts for 20 mol% of the total doping and the rest is due to chlorine ions. The ratio of the combined dopant ions to that

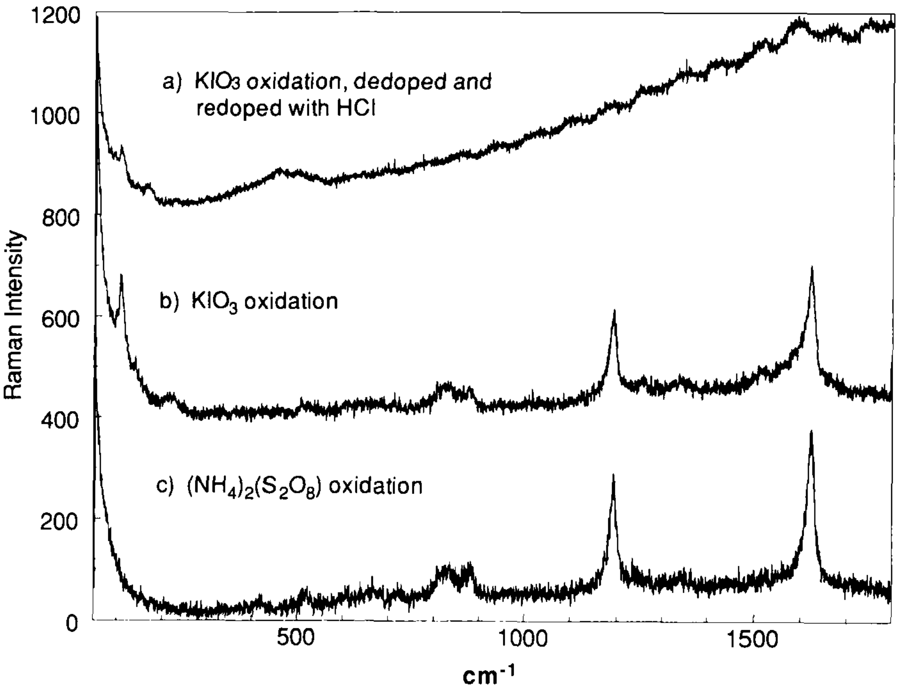


FIGURE 6 Raman spectra of the as-synthesized colloidal polyaniline (b), the bulk polymer dedoped and redoped with HCl (a) and the bulk polymer obtained with ammonium persulfate (c) for comparison.

of nitrogen (based on one nitrogen atom for each aniline monomer unit) is approximately 50 mol% in one case and 75 mol% in another case. This means that there is a counter-ion for each 2 aniline repeat units and three counter-ions for each four aniline repeat units respectively. However, the actual amount of iodine involved in the doping process is probably less than the value given above because (i) secondary ion mass spectroscopy analysis (SIMS) indicated that there is a small amount of iodine that reacted with the backbone forming C-I bonds, and (ii) XPS results suggested that the triiodide ions might have formed a complex with the steric stabilizer.

CONCLUSIONS

Chemical grafting of polyaniline onto the backbone of the polymeric surfactant is so far the only way to obtain colloidal forms of the conducting polymer. It is interesting to note that a small percentage of grafts of polyaniline yielded a conducting colloid with a conductivity similar to that of the bulk polymer. The chemical grafting technique offers the advantage, compared to physical adsorption in the case of polypyrrole, of forming more stable materials in which desorption of the steric stabilizers does not take place. Such a technique could be generalized for the derivatization and use of other polymeric surfactants toward better colloidal stability and ease of film formation.

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