

X-ray Photoelectron Spectroscopy Study of Bulk and Colloidal Polyaniline

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ABSTRACT: X-ray photoelectron spectroscopy (XPS) has been used to determine doping levels and the nature of doping species in bulk and colloidal polyaniline prepared in the presence of KIO_3 in acidic media. The results show that protonation/doping of polyaniline is due to both chlorine (as Cl^-) and iodine (as I_3^- and I_5^-), whose relative contents depend on the initial oxidant to monomer ratio. Although most of the chlorine and iodine are in the ionic form, the results indicate that covalent (C-Cl and C-I) bonding occurs and has been quantified. The core level spectrum of N 1s is deconvoluted, and the doping level is determined from the integrated intensity of the peak which corresponds to the protonated imine nitrogen. Due to high-vacuum conditions, deprotonation occurs, resulting in lower doping levels than those obtained by elemental analysis.

Introduction

Interest in polyanilines as conducting materials is due to its air stability and ease of fabrication. Because of the various potential applications of such materials, a large number of researchers have investigated the various facets relative to their characterization and understanding of their properties. Structural properties are among the important aspects of these materials that needed to be investigated, and several groups have done a good deal of work using several characterization techniques. Among the techniques used is X-ray photoelectron spectroscopy (XPS) that is normally very helpful in determining the nature of the various species and the nature of bonding in the polymer.

It has been established that polyaniline can be synthesized in various forms by chemical or electrochemical means. The properties of the polymer, particularly those obtained by chemical oxidation, are dictated by the experimental conditions such as polymerization media and their pH. The various forms of polyaniline obtained chemically or electrochemically have been studied in detail by various groups.¹⁻³ The polymers consist of poly(*p*-phenylene amine imine)s in which the oxidation state of the polymer can vary from the fully reduced poly(*p*-phenylene amine) or leucoemeraldine base to the fully oxidized poly(*p*-phenylene imine) or pernigraniline base. The 50% oxidized poly(*p*-phenylene amine imine) or emeraldine base is the material that has been investigated the most. Oxidation of leucoemeraldine base or protonation of emeraldine base in the presence of HCl results in the formation of the conducting material emeraldine hydrochloride salt. The structures of the four compounds described above are shown in Figure 1.

Our investigation of polyaniline was initiated to attempt the production of colloidal dispersions of polyaniline for processability reasons. The chemical oxidation route was chosen for this study, and therefore polymerization using the various oxidants as studied in the past,^{4,5} such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$, H_2O_2 , and KIO_3 , was attempted for this approach. As a result of this study, only KIO_3 was found to be appropriate for yielding dispersions without precipitation because of its relatively milder oxidative properties.⁶

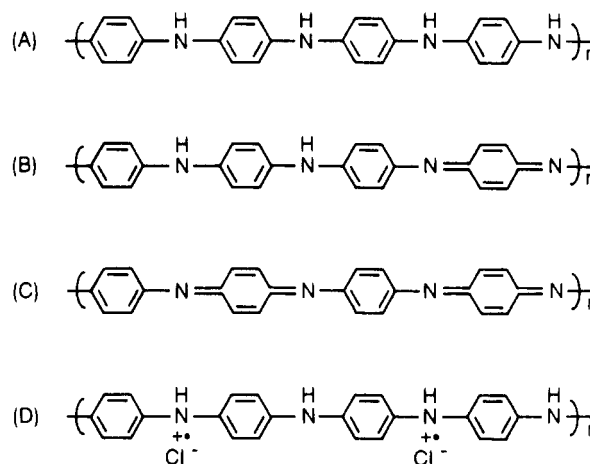


Figure 1. Various forms of polyaniline: (A) leucoemeraldine base, (B) emeraldine base, (C) pernigraniline base, and (D) emeraldine hydrochloride salt.

This polymerization was achieved successfully by graft copolymerization of aniline onto water-soluble steric stabilizers such as poly(vinyl alcohol-co-vinyl acetate), referred to as PVA in this paper, and poly(vinylpyridine)s, in an acidic medium (HCl) in the presence of KIO_3 . Thus, only the conducting form is obtained and studied here.

Due to the preparation conditions the subject materials contain chlorine and iodine as determined by elemental analysis. This adds to the complexity of the polymer, and therefore various techniques were used for their characterization, with the latest being XPS, which is the subject of this paper.

Experimental Section

The polymerization medium consisted of a 1.25 M HCl solution to which the appropriate amount of KIO_3 was added. Therefore, chlorine and iodine "doping" will be referred to in the Results and Discussion section as opposed to only chlorine "doping", which is the case when other oxidants are used. The steric stabilizer employed in this study is PVA. The preparation of bulk and colloidal polyaniline is described in detail elsewhere.^{7,8}

Conductivity measurements were performed using the four-probe technique on pelletized powders, except in the case of colloidal polyaniline, where films were used.

Table I
Effect of the Initial Oxidant to Monomer Ratio (r) on the Chemical Composition of Polyaniline, Its Doping Level, and Conductivity

r	N, wt %	Cl, wt %	I, wt %	[Cl]/[N]	[Cl] + [I]/[N]	$\sigma/(\Omega \text{ cm})^{-1}$
1	10.0	12.1	8.6	0.48	0.51	11.0
1.5	9.3	11.6	13.4	0.49	0.55	8.2
2.0	8.8	10.9	18.3	0.49	0.57	6.1
2.3	8.4	10.6	20.7	0.50	0.59	4.3
2.3 ^a	6.9	7.9	20.2	0.45	0.56	0.2
2.5	8.3	9.8	23.9	0.48	0.58	2.7
3.0	7.5	9.7	28.8	0.50	0.64	1.9

^a Colloidal polyaniline.

XPS measurements were performed on a Physical Electronics 548 photoelectron spectrometer with a Mg K α X-ray source (1253.6-eV photons). The X-ray power supply was run at 10 kV and 20 mA. Pressure in the analysis chamber was in the 10^{-8} – 10^{-10} Torr range. The samples were mounted onto the sample holder by means of a double-side adhesive tape. All core level spectra were referenced to the C 1s neutral carbon peak at 284.6 eV.

Results and Discussion

We have used in the past several techniques for the characterization of polyaniline prepared by the KIO₃ oxidation route in the bulk and colloidal forms. A good understanding of certain aspects has been achieved. However, the structural properties proved to be more difficult to determine because of the complexity of our system. In addition to partial protonation of polyaniline achieved normally in the presence of the acid HCl, iodide species are present and interact with the system, resulting in iodine-doping and side reactions. Furthermore, the colloids contain an additional element which is the steric stabilizer that could interact with the various species formed as a result of the doping process.

To shed some light on the various processes, we have analyzed our results in light of what is known in the literature on polyaniline prepared by the more common route which utilizes ammonium persulfate as oxidant or by anodic oxidation as studied by several groups.^{9–13}

In this paper, we report the results obtained on samples prepared using initial oxidant to monomer molar ratios (referred to as r) between 0.17 and 0.5 or ratios between 1 and 3 when the number of electrons (6 electrons according to refs 4 and 7) involved in the oxidation process is taken into account.

Because composition is one of the issues addressed here, it is of importance to report the elemental analysis results reported earlier⁷ in a way that reflects the level of doping. In Table I are reported the relative weights of nitrogen, chlorine, and iodine obtained by microanalysis. The level of doping was calculated and reported in two separate columns which consist of the molar ratio of chlorine to nitrogen and the molar ratio of the sum of chlorine and iodine to nitrogen assuming that the iodine species responsible for doping is I₃[−]. This assumption is based on unpublished results from Raman scattering experiments which indicated the presence of triiodides and a small fraction of pentaiodides. Other species such as unreacted IO₃[−], undetected in the Raman spectra, might be present as dopant anions. The conductivity of the various compounds is reported also for comparison in later discussions.

The molar ratios indicate that nearly 50% protonation is due to the hydrochloric acid and that additional doping, which increases with the ratio r , takes place. Although oxidation caused by the combined effects of chlorine and iodine is higher than 50% (moving in the direction of

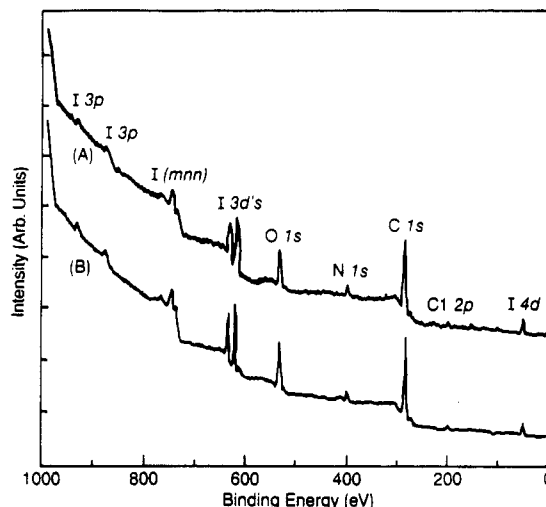


Figure 2. Full XPS spectra of bulk (A) and colloidal polyaniline (B) prepared with a ratio r of 2.3.

pernigraniline formation), the conductivity seems to be comparable to the commonly obtained emeraldine hydrochloride salt. As the combined doping increases, the conductivity decreases as expected. In all cases, the doping level is probably exaggerated due to trapped HCl and I₂ that can be removed, as we observed in our experiments, under dynamic vacuum.

When subjected to high-vacuum conditions such as those in which the XPS experiment is conducted, the amount of chlorine and iodine is likely to be decreased. A reduction of the content of chlorine in emeraldine hydrochloride is known to occur.¹² We have observed similar reductions in our XPS experiments of the chlorine and iodine contents. Therefore, the quantitative results which will be reported later will not reflect the stoichiometries measured in the as-synthesized materials which are reported in Table I. The nature of species that exist in the system which we wanted to determine is however unchanged. As will be mentioned later, covalently bonded iodine and chlorine to the ring (although in small amounts) might account partially for the high doping levels. The presence of covalently bonded halogens in polyanilines has been reported earlier.^{14,15}

In Figure 2, we show the full XPS spectrum of the bulk material prepared with a ratio r of 2.3 (A) and of the colloidal material prepared at the same ratio (B) as examples. The composition of the material consists, as expected, of carbon, nitrogen, chlorine, and iodine. In addition to the elements of polyaniline, an intense peak of oxygen O 1s is observed in all samples at binding energies (BE's) in the range 530–532 eV. It is common to have oxygen incorporated in the polymer during the oxidative polymerization. In the case of the colloidal material, a contribution to the oxygen peak is due to the steric stabilizer which contains alcohol and acetate moieties. At high initial oxidant contents ($r = 3$), the oxygen peak in the bulk polymer consists of two components which could be attributed to free unreacted oxidant and oxygen bound to the polymer. The oxygen line is known to fall around 533 eV within a narrow range of approximately 2 eV. The extremes are usually seen in carboxyl and carbonate groups in which the singly bound oxygen has the higher BE. The oxygen peak in our samples is shifted to lower BE's which indicates that the oxygen species are ionic in nature, with those at higher BE's being due to polar oxygen bonds in unreacted IO₃[−]. XPS integrated intensities of oxygen and iodine peaks in bulk polyaniline prepared with a ratio r of 2.3 give a molar ratio [O]/[I] of 2.8. This ratio increases

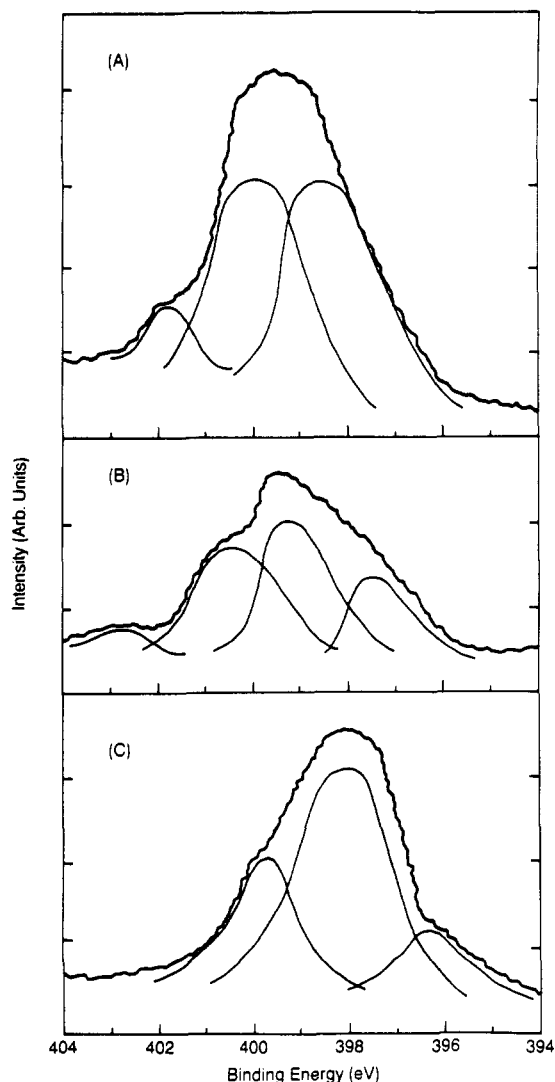


Figure 3. Core level spectra of N 1s for bulk polyaniline prepared with $r = 1$ (A) and $r = 3$ (B) and for the colloidal form ($r = 2.3$) (C).

to 6.6 in the colloidal sample due to the steric stabilizer. Based on this, the oxygen content in bulk polyaniline seems to be due mostly to IO_3^- in unreacted KIO_3 or as a possible dopant anion. As indicated on the spectrum, the iodine peaks consist of 3p's, 4d, 3d's, and the Auger peak (MNN). The intensity of the chlorine 2p peak is relatively small due to high-vacuum conditions under which a large amount of chlorine in the surface of the sample has been depleted. For example, XPS analysis of the colloidal sample resulted in a molar ratio of chlorine to nitrogen of 0.13 as opposed to 0.45 by elemental analysis.

In this study, we focus on the core level spectra of C 1s, N 1s, Cl 2p, and I 3d. The shape and morphology of the spectra of C 1s and N 1s are influenced by the presence of chlorine and iodine and the proportion of the two latter components.

Core Level Spectra of N 1s. As shown in Figure 3, the main peak is usually wide and shows clear splitting due to the various amine and imine species similarly to what was reported earlier.⁹⁻¹³ Three characteristic spectra are shown in Figure 3 for bulk polyaniline prepared using ratios $r = 1$ (A) and $r = 3$ (B) and colloidal polyaniline (C). In all cases, the main peak is deconvoluted into three components attributed to nondoped imine ($=\text{N}-$), and doped imine (N^{++}) at BE's of 398, 399.5, and 402 eV, respectively, and whose relative intensities were derived from the integrated intensities of the peaks.

Table II
Effect of the Initial Oxidant to Monomer Ratio (r) on the Relative Contents of the Various Nitrogen Species As Determined by the Integrated Intensities of the XPS Nitrogen 1s Lines

r	$=\text{N}-$ % (398 eV)	$-\text{NH}-$ % (399.5 eV)	N^{++} % (402 eV)
1.0	45	45	10
3.0	30	45	25
2.3 ^a	16	62	22

^a Colloidal polyaniline.

A slight shift is observed in BE of the main peak when varying the oxidant content. The relative content derived from the integrated intensities of each component has been found to vary with the amount of iodine as shown in Table II. The relative content of the charged imine species increases as r increases. This indicates that the iodine species provide for an additional doping to that attributed to chlorine. The colloidal material which is prepared at a ratio r of 2.3 has the same doping level as that of the bulk material whose ratio r is 3.

It has been noted¹¹ that protonation reduces the full width at half-maximum (fwhm) of the nitrogen peak from 2.4 to 2.0 eV. The larger values we observe here demonstrate that our system is perhaps relatively less protonated than that prepared using ammonium persulfate oxidant.

However, because conductivities of the various materials are comparable to those obtained on other polyanilines, the most logical explanation at this point, as will be shown later, is that the coexistence of complexes between N^{++} , Cl^- , I_3^- , and I_5^- and their competing interactions are responsible for the large width, which is approximately 3.5 eV. The colloidal material exhibits a peak whose fwhm is 2.9 eV. A reduced interaction of the iodine species with the imine nitrogen due to the presence of the steric stabilizer might be responsible for that.

It is worth noting that there is no evidence for any N-Cl linkages as suggested by Tan et al.¹¹ Such linkages would be the result of overoxidation and would appear at higher BE's that are not present in our spectra. Linkages with iodine are even less likely to occur.

Core Level Spectra of C 1s. As shown in Figure 4, the carbon peaks are slightly asymmetric and wide compared to a typical conjugated carbon backbone. Although there are various carbon bondings in the polymer, the peaks do not exhibit additional features in comparison with that of nitrogen. As suggested earlier,¹³ the line is asymmetric due to the loss of charge to the dopant as a result of protonation. The extent of asymmetry is a qualitative indication of how conductive the system is. The shape of the peak is unaffected by varying r . The difference in the conductivity between the various samples (see Table I) is not sufficient to incur significant changes in the peak's symmetry. The partial loss of asymmetry is due in part to the high-vacuum environment which results in the partial loss of chlorine and iodine during the XPS experiment. For example, the colloidal sample whose molar ratio of chlorine to nitrogen was found to be 45% by elemental analysis prior to the XPS experiment gave a ratio of 13% by XPS.

As observed in the case of polyacetylene,¹⁶ the carbon peak is shifted to a higher BE due to the charge transfer from the polyaniline moiety to the iodine and chlorine dopants. The shift varies with r which is indicative of the extent of delocalization. Shifts to 0.3, 0.6, 0.6, 1.1, 1.2, and 0.9 eV are obtained for ratios (r) of 1.0, 1.5, 2.0, 2.3, 2.5, and 3.0, respectively. A small shift of 0.4 eV is obtained in the case of the colloidal material ($r = 2.3$).

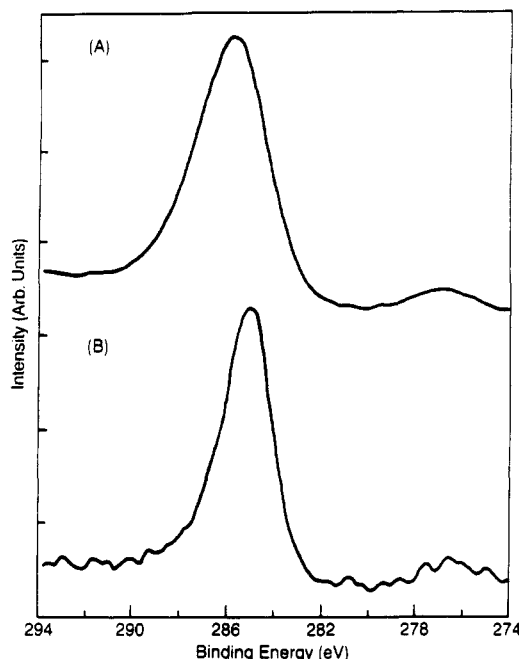


Figure 4. Core level spectra of C 1s for bulk (A) and colloidal polyaniline (B) both prepared with a ratio r of 2.3.

Although the higher r materials are less conductive, their higher shift indicates that a more delocalized system is observed. This can be explained by the fact that iodine, which becomes more predominant as r increases, is a less efficient dopant than chlorine as will be discussed later.

The peaks are unusually wide with an fwhm of 3.0 eV, except for the colloid (2.5 eV), compared to 1.3 eV for polyacetylene,¹⁶ but comparable or slightly higher than those observed in sulfonated polyaniline.¹³ Such an increase is probably due to the interactions of various species of iodine and chlorine and the covalent bonding with nitrogen and, to a small extent, to the covalent bonding with chlorine and iodine. Because the primary shift of C 1s due to covalent chlorine and iodine in an aromatic system is less than 1 eV, it would be difficult to estimate the amount of covalent bonding from the carbon spectrum, particularly when it is relatively small.

Shake-up satellite peaks which are normally observed at less than 10-eV separation from the main peak toward higher BE's for aromatic systems are not observed. Because they are assigned normally to the π - π^* transition,^{17,18} the absence of shake-up peaks indicates that charge transfer is predominant in the polyaniline moiety.

Core Level Spectra of Cl 2p. The degree of protonation of polyaniline prepared using ammonium persulfate is normally derived based on the chlorine content that is determined by elemental analysis. In our case, protonation takes place in the presence of both chloride and iodide species which are competing in the protonation process. Analysis of the chlorine content before and after the XPS experiment in several samples indicated that there is a weight loss due in part to reduction of the chlorine content. Therefore, it is difficult to determine the exact content of chlorine and correlate it to the conductivity measured in ambient conditions. However, XPS results as shown in Figure 5 indicate that the chlorine main peaks can be deconvoluted easily into two main components assigned to two chloride ions that differ in the strength of their interaction with the imine nitrogen as noted by Epstein et al.¹³ The two peaks have been assigned in the literature to Cl 2p^{1/2} and Cl 2p^{3/2}, with the latter peak at higher BE's.¹⁹ In addition to the two main

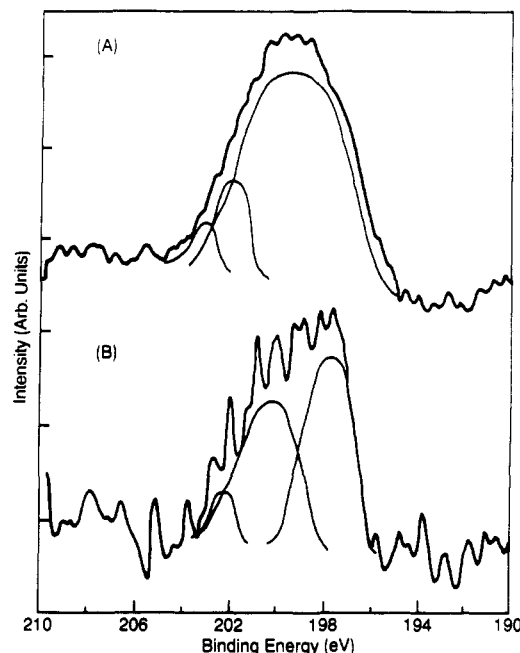


Figure 5. Core level spectra of Cl 2p for bulk (A) and colloidal polyaniline (B) both prepared with a ratio r of 2.3.

Table III
Effect of the Initial Oxidant to Monomer Ratio (r) on the Relative Contents of Cl 2p Components

r	% 2p ^{3/2} (≈ 199 eV)	% 2p ^{1/2} (≈ 201 eV)	% covalent Cl (≈ 203 eV)
1.0	66	32	2
1.5	75	19	6
2.0	76	18	5
2.3	80	16	4
2.3 ^a	65	27	8
2.5	80	15	5
3.0	90	9	1

^a Colloidal polyaniline.

components, we observe that at higher BE's covalent chlorine is present.

Deconvolution of the main peak resulted therefore in the following three components: the 2p^{3/2} component around 199 eV, the more localized 2p^{1/2} component around 201 eV, and the covalent chlorine component around 203 eV. The BE's mentioned above are approximate numbers because the peak position of each component varies slightly with r in a random way. The contributions of each component to the main peak are shown in Table III.

The data show that the content of covalent chlorine is in the range of 1–10%. Although in some cases the amount of covalent chlorine is small, it has been detected in our samples with the tendency of increasing as the amount of oxidant decreases. The covalent bonding is attributed to C–Cl rather than N–Cl bonding as suggested by Tan et al.¹¹ The large amount of covalent chlorine in their 44%-protonated emeraldine (23% of the total chlorine peak) particularly when bonded to nitrogen seems unrealistic because the system would not be as conductive as reported.

At high ratios ($r = 3$), the chloride ion is less likely to overoxidize the aniline moiety due to the competing interactions by iodide ions, thus resulting in low levels if any of covalent chlorine. In the case of the colloid, the larger contribution of covalent chlorine to the main peak is due to the presence of the steric stabilizer which may be chlorinated in addition to the chlorination of the benzene ring in polyaniline. The Cl 2p peak for poly(vinyl chloride) is known to occur at 199.9 eV.⁹

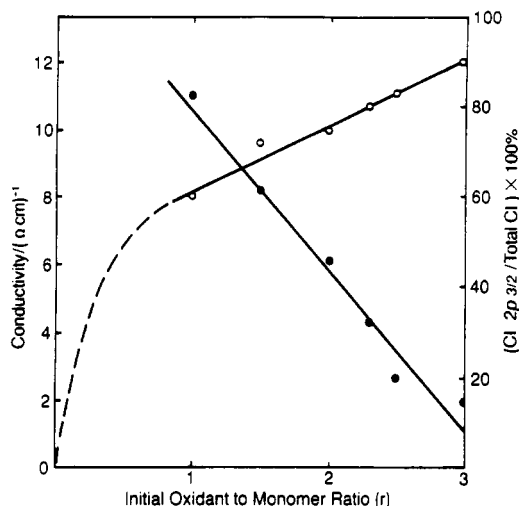


Figure 6. Effect of the initial oxidant to monomer ratio (r) on the relative content of the $2p_{3/2}$ component in the Cl $2p$ peak (O) and on room-temperature conductivity (●).

In Figure 6, we plot the percentage of $2p_{3/2}$ and room-temperature conductivity (before XPS) as a function of r . The relative amount of $2p_{3/2}$ increases linearly in the range of r studied here (1.0–3.0). The small change in the conductivity can be attributed to the fact that the interaction of iodides with the imine nitrogen increases with r and that the conductivity is no longer attributed to chloride dopant anions only but also to iodide dopant anions which are less efficient dopants than the former in polyaniline.

As observed in the case of other core level peaks, the chlorine peak of the colloid is narrower than that of the bulk material. The Cl $2p$ peaks are wider than those reported in the literature due to covalently bonded chlorine and the various interactions of Cl^- with other species in the system, particularly those derived from the oxidant KIO_3 .

Core Level Spectra of I 3d. The portion of the spectrum relative to iodine 3d has two peaks that are assigned to $3d_{5/2}$ around 620 eV and $3d_{3/2}$ around 632 eV with a constant shift of 11.5 eV, as expected, between the two peaks in all samples. The spectra are compared to the iodine shift observed in the reference compound CsI_3 which is known²⁰ to contain only I_3^- . The ratio of the peak intensities of $3d_{5/2}$ to $3d_{3/2}$ is approximately 5/3 as expected.

Both peaks in all samples can be deconvoluted, as shown in selected spectra in Figure 7, into three peaks: (i) pentaiodide I_5^- around 619 eV; (ii) triiodide I_3^- around 620 eV; and (iii) covalent iodine C–I around 623 eV. These assignments are based on a CsI_3 reference compound and the observations made on iodine-doped polyacetylene.^{16,21–23}

The relative content of the various iodine species has been determined for all samples and seems to be independent of the oxidant to monomer ratio. An average relative content was determined to be 85% I_3^- , 10% I_5^- , and 5% covalent iodine. This indicates, as was observed for polyacetylene, that both species, I_3^- and I_5^- , contribute to the doping process and that I_3^- is the predominant one. It was suggested that I_5^- is the result of the association of I_3^- and I_2 .²¹ Raman scattering experiments on our polyanilines indicated that the two ionic species are present. The covalent bonding C–I has been shown to exist in our materials by secondary ion mass spectroscopy (SIMS).²⁴

We have observed a shift to higher BE's in all bulk polyaniline samples relative to the peaks in CsI_3 of approximately 0.6 eV for $3d_{5/2}$ and 0.7 eV for $3d_{3/2}$. This

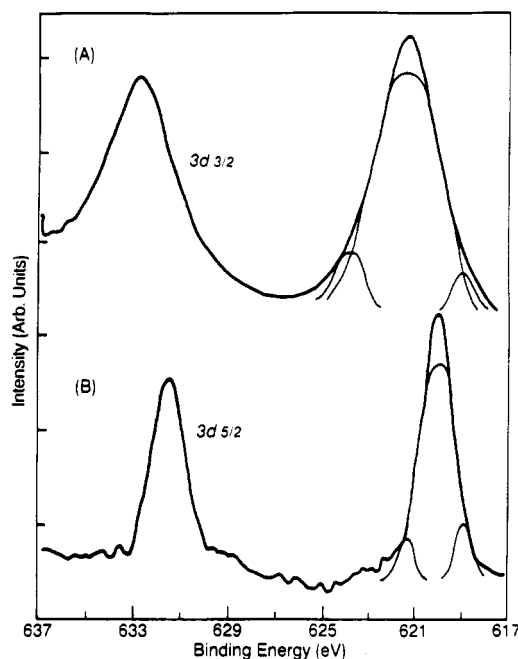


Figure 7. Core level spectra of I 3d for bulk (A) and colloidal polyaniline (B) both prepared with a ratio $r = 2.3$.

demonstrates that the N^+I_3^- complex is more localized than in Cs^+I_3^- . The shift in the case of the colloidal material is unusually low (0.1 eV) for both peaks.

The peak widths (fwhm) are 3.1 and 3.2 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively. The colloidal sample has narrower peaks (1.6 eV for both peaks). This difference might be due to the large amount of unreacted oxidant in the bulk polymer as was suggested earlier in the discussion relative to O 1s core level spectra.

Here again, the high-vacuum conditions gave lower amounts of iodine as determined by the integrated intensities of XPS peaks compared to that given by elemental analysis. For example, as determined by the latter technique, the colloidal material has a molar ratio of iodine to nitrogen of 32%, or 10.8% if we use the approximation in which I_3^- only is present. The XPS results show that this ratio is reduced to 9.9%, with the I_5^- species being the more likely one to be lost under vacuum because of the weak complex between I_3^- and I_2 . The partial loss of iodine and chlorine account for the weight loss measured on the sample studied by XPS.

Conclusion

Structural studies of bulk and colloidal polyaniline prepared in the presence of KIO_3 using XPS have shown that the doping process is more complex than in materials prepared using other oxidants, and therefore conduction mechanisms and dopant-induced structural changes could be different. The advantage of KIO_3 is due to its relatively mild oxidative properties and thus is the only one that leads to the formation of colloidal dispersions of polyaniline. However, because of the resulting iodine species and their doping capability, competing interactions with the imine nitrogen vis-à-vis chloride ions exist and the determination of the real level of protonation as well as the nature of the doping species becomes more difficult. The real contribution to the conductivity of chlorides and iodides is not really known, and the doping efficiencies differ for both dopants. Also, side reactions alter the reactivity of polyaniline toward protonation and thus the formation of polarons on the imine sites (N^+). Further-

more, partial loss of the dopant due to the high vacuum of XPS experiments might alter the equilibrium of the various ionic species, particularly in the case of iodine.

The results, however, show the nature of all the species and side reactions involved. Also, the results indicate that the various species can be quantified in a relative manner, assuming that a stable composition is obtained after pumping the samples under high vacuum and that the nature and relative content of each species is being preserved.

Thus, our experiments indicate that chloride ions are more effective as dopants than iodides which tend to over-oxidize the polymer toward the formation of pernigraniline, which is the oxidized form of polyaniline. This suggests that lower oxidant to monomer ratios are better. Higher conductivities are consequently obtained at lower ratios, but, at the same time, lower polymerization yields are obtained.

Although the extent of covalent iodine and chlorine is relatively small, it could have an effect on the conductivity. However, it was reported earlier^{14,15} that the presence in small quantities of covalently bonded halogens did not result in a decrease in the conductivity. Nevertheless, such side reactions should be minimized or avoided. This might be achieved by carrying out the polymerization at lower temperatures than the commonly employed ambient temperature.

As observed earlier, all core level peaks of the colloidal material are narrower than their bulk material counterpart without altering the nature of relative content of each component in each peak. This is probably due to the smaller number of species relative to each element and also due to the fact that the dopant interacts with the steric stabilizer, thus reducing the actual amount that is effectively in interaction with polyaniline. Furthermore, the high surface area of the composite created by the presence of the steric stabilizer makes removal of chlorine and iodine easier than in the bulk polymer under the XPS vacuum conditions.

On the basis of the above conclusions, it appears imperative that materials of this nature should have a high purity by removal of unreacted species and be submitted to high-vacuum conditions for removal of any excess of dopants in order to achieve a stable composition that can be analyzed with a good reproducibility by surface techniques such as XPS.

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