

X-ray photoelectron spectroscopy studies of the chemical structure of polyaniline

K. L. Tan and B. T. G. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

E. T. Kang and K. G. Neoh

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511

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X-ray photoelectron spectroscopy (the deconvoluted high-resolution N 1s core-level spectrum in particular) was used for the quantitative determination of the proportion of benzoid amine, quinoid imine, and protonated units in chemically synthesized polyaniline. This method allows the tracking of structural changes during polyaniline oxidation and reduction.

INTRODUCTION

The aniline family of polymers has been known for nearly a century,¹ but has only recently been the subject of renewed interest.² The polymers are basically poly(paraphenylene amine imines)³ in which the oxidation state of the polymer can vary from the fully reduced poly(paraphenylene amine) or "leucoemeraldine" to the fully oxidized poly(paraphenylene imine) or "pernigraniline." The 50% oxidized poly(paraphenylene amine imine) has been termed "emeraldine base." The electronic structure of these polymers can be varied by either electrochemical doping⁴ or protonation.⁵ The latter occurs preferentially at the imine repeating units.² The chemical structures of polyaniline have been studied extensively, for example, by infrared (ir) spectroscopy,⁶⁻⁸ x-ray photoelectron spectroscopy (XPS) (Refs. 9-12) and ¹³C NMR (Ref. 13) and by the studying of model compounds.^{14,15} However, the chemical structure associated with a particular redox state, such as the proportion of quinoid imine, benzoid amine, and positively charged nitrogen, has yet to be determined quantitatively and unambiguously. This work demonstrates that the three nitrogen species can be quantitatively differentiated by the XPS technique.

EXPERIMENT

Polyemeraldine hydrochloride was synthesized at 0-5°C from aniline and ammonium persulphate in 1M aqueous hydrochloric acid solution.^{5,16} It was converted to emeraldine base or deprotonated to various extent by treatment with varying amounts of 0.5M aqueous NH₄OH or NaOH. The emeraldine based was reprotonated to polyemeraldine hydrochloride or products with intermediate oxidation states by equilibrating the emeraldine base in HCl solution by varying initial concentration. The fully reduced polyleucoemeraldine was obtained by treatment of emeraldine base with excess phenylhydrazine according to the method of Green and Woodhead.¹

XPS measurements of the various polymer samples were made on a VG Scientific ESCALAB MkII spectrometer with a Mg K α x-ray source (1253.6-eV photons). All samples were ground into fine powder before being

mounted on standard sample holders by means of double-sided adhesive tapes. The x-ray power supply was run at 12 kV and 10 mA. Pressure in the analysis chamber during the measurements was typically 10⁻⁸ mbar or below. All core-level spectra were referenced to the C 1s neutral-carbon peak at 284.6 eV. The peak area ratios for the various elements were corrected by experimentally determined instrumental sensitivity factors and may be subjected to $\pm 10\%$ error. Each spectrum was fitted with Gaussian component peaks. The peak width full width at half maximum (FWHM) was maintained constant for all components in a particular spectrum.

RESULTS AND DISCUSSION

Earlier XPS studies show that the N 1s core-level spectrum of the polyemeraldine base consists of one spectral peak with a linewidth (FWHM) on the order of 2.4 eV.^{9,10} Upon protonation with HCl, the linewidth is substantially reduced¹⁰ and a high-binding-energy (BE) shoulder or tails becomes prominent.^{9,11}

Figure 1(a) shows the N 1s core-level spectrum for the polyemeraldine base obtained in the present work. The spectrum is deconvoluted into two major component peaks centered at 399.3 ± 0.1 and 398.1 ± 0.1 eV and with a linewidth of 1.65 eV. The two peaks are assigned to the amine and imine structure, respectively, based on the following supporting evidence. Comparison of the N 1s peak BE of pyridinium nitrogen in polyvinylpyridine (=N- structure) with that of the pyrrolylium nitrogen in polypyrrole¹⁷ (-NH- structure) suggests that the former is lowered by about 1.1 eV (398.4 vs 399.5 eV, based on neutral C 1s peak at 284.6 eV). Furthermore, in polypyrrole complex, dehydrogenation of a certain fraction of pyrrolylium nitrogen, followed by rearrangement of the pyrrole bonds to satisfy the three nitrogen valences has resulted in a more electron-rich nitrile or aza-type nitrogen species and a corresponding negative shift of the N 1s BE by about 1.3 eV.^{18,19}

The two major peak components in Fig. 1(a) are of about the same area, suggesting that about equal amounts of quinoid imine and benzoid amine structure are present in the polyemeraldine base. This is entirely consistent

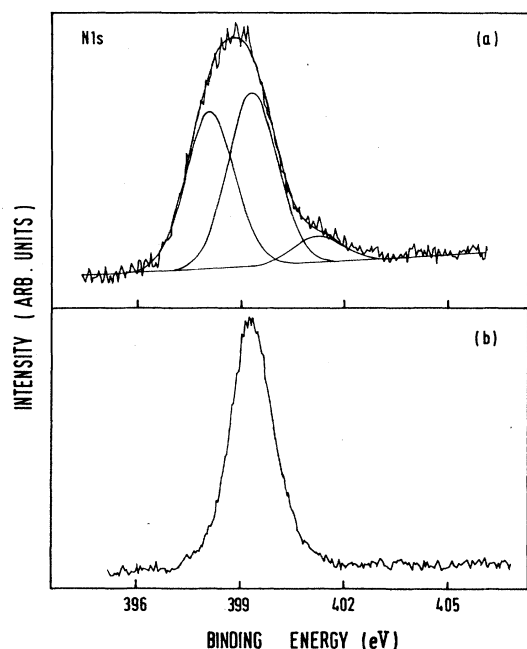


FIG. 1. N 1s XPS core-level spectra of (a) polyemeraldine base and (b) fully reduced polyleucoemeraldine.

with the polyemeraldine structure proposed by MacDiarmid *et al.*² The slightly lower amount of imine structure observed is probably associated with the presence of a trace amount of positively charged nitrogen, as indicated by the residual N 1s high-BE tail and the presence of trace amount of chloride anions in the Cl 2p core-level spectrum of the sample. Nevertheless, this is consistent with the reports^{2,5} that protonation occurs mainly at the imine units.

Figure 1(b) shows the N 1s XPS core-level spectrum of the fully reduced polyleucoemeraldine which consists of only benzoid rings and amine nitrogen.²⁰ As expected, the N 1s core level has only a single environment. Furthermore, the spectrum shows a peak BE at 399.3 eV with a linewidth of only about 1.45 eV. This is in excellent agreement with the peak assignments made in Fig. 1(a). The predominantly benzoid amine structure in the present polyleucoemeraldine can probably be used to give partial support to the infrared absorption spectroscopy of Tang *et al.*⁸ The ir absorption spectrum of polyemeraldine base shows two absorption bands of about equal magnitude at ca. 1590 and 1500 cm^{-1} . The respective bands have been

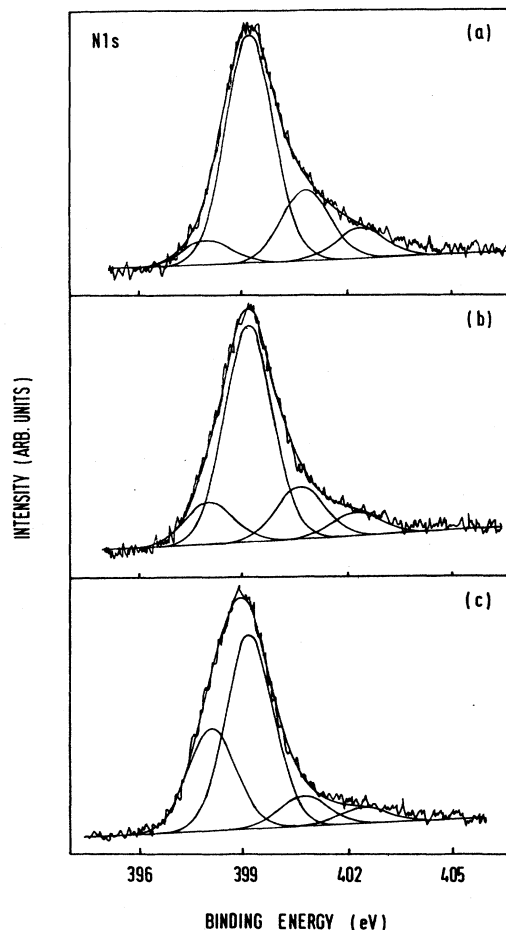


FIG. 2. N 1s XPS core-level spectra of polyemeraldine hydrochloride at various degree of protonation: (a) total $[\text{Cl}]/[\text{N}] = 0.44$, (b) total $[\text{Cl}]/[\text{N}] = 0.28$, and (c) total $[\text{Cl}]/[\text{N}] = 0.14$.

attributed to the absorption of quinoid and benzoid units.⁸ The ir absorption spectrum of the present polyleucoemeraldine shows a substantially enhanced absorption at 1500 cm^{-1} while the band at 1590 cm^{-1} and attributable to the quinoid structure⁸ has disappeared almost completely.

It has been well established in the literature^{2,5} that the imine nitrogens of polyemeraldine base are preferentially protonated by HCl. Thus, in the protonated polyemeraldine

TABLE I. XPS experiment results and surface stoichiometries for the partially deprotonated polyemeraldine hydrochloride.

Sample	XPS surface stoichiometries totals			N 1s Core-level spectrum			Conductivity σ (S/cm)
	$[\text{Cl}]/[\text{N}]$	$[-\text{Cl}]/[\text{N}]$	$[\text{Cl}^-]/[\text{N}]$	=N- (BE = 398.1 ± 0.1 eV)	-NH- (BE = 399.3 ± 0.1 eV)	N ⁺ (BE ≥ 401 eV)	
a	0.44	0.10	0.34	0.06	0.64	0.30	1.0
b	0.28	0.10	0.18	0.14	0.64	0.22	10^{-2}
c	0.14	0.06	0.08	0.31	0.57	0.12	10^{-4}

dine hydrochloride structure, the N 1s peak component due to the imine at 398.1 eV should have been shifted to a substantially higher BE. Figure 2(a) shows that curve fitted N 1s spectrum of a polyemeraldine hydrochloride sample with an XPS determined elemental [Cl]/[N] ratio of 0.44. The imine peak component has disappeared almost completely and a high-BE shoulder, attributable to positively charged nitrogen,^{9,11} becomes prominent. Upon deprotonation of this sample with various amounts of NaOH, the imine structure gradually recovers while the high-BE shoulder decrease steadily. The N 1s spectra for two of the partially deprotonated samples are shown in Figs. 2(b) and 2(c). The corresponding XPS experimental results for all three samples at various levels of protonation are summarized in Table I.

In all of the present complexes, the fraction of positively charged nitrogen appears to be substantially lower than the amount of protonation determined from total [Cl]/[N] balance. Similar observation has also been reported, for example, in electrochemically synthesized polyaniline films,¹¹ in which the positive shoulder constitutes only 20% of the total N 1s area at a [Cl]/[N] ratio of 0.6. The Cl 2p core-level spectrum for all of the present complexes suggests the presence of two major components at about 197.2 and 200.1 eV which can be attributed to the chloride anion and covalent chlorine, respectively. The presence of the latter has also been observed earlier.¹² Figure 3 shows the Cl 2p core-level spectrum for the present polyemeraldine hydrochloride sample with a [Cl]/[N] ratio of 0.44. Thus, the degree of protonation cannot be determined based on the total Cl balance alone. The data in Table I indicate that a close balance in charges can indeed be observed based on the amount of positively charged nitrogen and the actual amount of chloride anion present. The presence of localized unit positive charge on the nitrogen has been favored by Munro, Parker, and Eaves¹¹ and is consistent with the concept of nitrogenonium ion polymer of MacDiarmid *et al.*,² although other studies suggest the presence of delocalized radical cations in aniline oligomers¹⁵ and electrochemically prepared polyaniline.¹⁰

Based on the present peak assignments, Fig. 2 and Table I suggest the presence of a relatively high proportion of amine structure in all of the protonated samples, especially at high protonation levels. This is consistent with the single narrow N 1s peak at 399–400 eV observed by other investigators in the fully protonated samples.^{10,11} Thus, some of the imines must have been transformed into

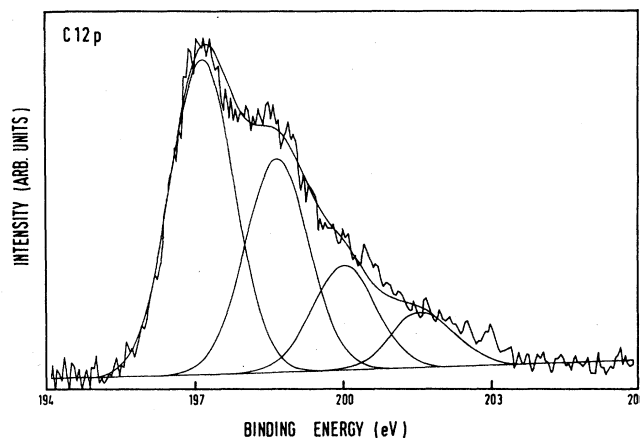


FIG. 3. Cl 2p XPS core-level spectrum of polyemeraldine hydrochloride with total [Cl]/[N] = 0.44.

the amine structure, probably through the addition of HCl to the quinoid units. This also helps to account for the presence of covalent chlorine. An earlier study¹² has shown that treatment of *N,N'*-diphenyl-*p*-quinonediimine model compound with concentrated HCl resulted mainly in covalently bonded chlorine, while mainly ionic chlorine was observed when *N,N'*-diphenyl-*p*-phenylenediamine was treated. Furthermore, the ir data of Tang *et al.*⁸ suggest qualitatively that the quinoid-to-benzoid ratio decreases with increasing HCl concentration and the phenomena has been attributed to the 1,4 addition of HCl to the quinoid units. Finally, the data in Table I indicate that the reduction in covalent chlorine occurs only at a high degree of deprotonation and is accompanied by a corresponding reduction in amine structure.

CONCLUSION

It was demonstrated that the imine, amine, and protonated nitrogens of polyaniline at various states of oxidation and reduction can be differentiated and determined quantitatively from the high-resolution N 1s XPS core-level spectrum. The physicochemical nature of protonation of polyaniline by HCl was also revealed in the XPS study.

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