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## **STRUCTURAL STUDIES OF ANILINE: SUBSTITUTED ANILINE COPOLYMERS BY XPS**

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### **ABSTRACT**

The structure and protonation level of the chemically synthesized 2-chloroaniline and 2-iodoaniline homopolymers and their copolymers with aniline have been studied. The results indicate there is no elimination of the substituent group and the polymerization probably occurs at the para-position. The protonation level of the copolymers decreases substantially when the fraction of substituted aniline units is above 0.5, and the electrical conductivity of the copolymers decreases rapidly with an increase in the fraction of substituted aniline units. The protonation level is also lower when HCl rather than H<sub>2</sub>SO<sub>4</sub> is used as the protonating acid species, and a significant fraction of the chlorine incorporated is covalently bonded to the polymer. The N1s core-level spectra of the copolymer and the haloaniline homopolymer bases reveal that their imine/amine ratio is substantially lower than that of the polyaniline base. The copolymers show partial solubility in chloroform, but the electrical conductivity of the chloroform-treated samples is not significantly different from that of the pristine sample. When the copolymers

synthesized in HCl are heated to 150°C, a fraction of the ionic chlorine is converted to covalently bonded species, resulting in a substantial decrease in the electrical conductivity.

## INTRODUCTION

The aniline family of polymers is basically poly(paraphenylene amine-imine) [1] in which the oxidation state can be varied from the fully reduced poly(paraphenyleneamine) or "leucoemeraldine" to the fully oxidized poly(paraphenyleneimine) or "pernigraniline." Conductive polyaniline is usually prepared by the oxidative polymerization of aniline in HCl by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  to yield emeraldine hydrochloride [2]. Treatment of the emeraldine hydrochloride with  $\text{NH}_4\text{OH}$  converts it to the insulating state, "emeraldine base," which corresponds to 50% oxidized poly(paraphenyleneamineimine) [3]. When emeraldine base is equilibrated in a large excess of aqueous HCl, protonation occurs preferentially at the imine repeat units to yield emeraldine hydrochloride [3].

Recently, a number of studies have reported on the use of electron spectroscopy for chemical analysis (ESCA) or x-ray photoelectron spectroscopy (XPS) for investigating the structure of polyanilines synthesized by both chemical and electrochemical methods [4-8]. The structures of electrochemically synthesized halogen-substituted polyanilines [7] and chemically synthesized poly(*o*-chloroaniline) and poly(*m*-toluidine) [9] have also been investigated. We have recently demonstrated that the chemical structure associated with a particular redox state of polyaniline, such as the proportion of quinoid imine, benzoid amine, and positively charged nitrogen, can be quantitatively determined by XPS [10]. In the present XPS study we investigate the structural changes associated with the chemical copolymerization of aniline and its halogen-substituted derivatives. Since the electrical conductivity of polyanilines is related to the protonation level, the emphasis of this study will be on the oxidation state and protonation level of the copolymers and how these may differ from the homopolymers.

## EXPERIMENTAL

Experiments with the halogen-substituted monomers (chloroaniline, bromoaniline, and iodoaniline) show that these monomers can be polymerized in an acidic medium with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as oxidant. However, the

yield is dependent on the halogen substituent and its position on the ring as well as the acid medium. Since the *ortho*-haloanilines give a substantial yield of product when polymerized in either HCl or H<sub>2</sub>SO<sub>4</sub>, the copolymerization experiments were carried out with aniline and either 2-chloroaniline or 2-iodoaniline. The mole ratio of chloroaniline or iodoaniline to aniline in the reaction mixture ranged from 0.2 : 1 to 2 : 1, and the monomer: (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> ratio was kept constant at 1 : 1. The copolymerization of chloroaniline with aniline was carried out in 1 M H<sub>2</sub>SO<sub>4</sub> instead of HCl so that the fraction of chloroaniline in the copolymer could be estimated from the chlorine content. The copolymerization of iodoaniline with aniline was carried out in both H<sub>2</sub>SO<sub>4</sub> and HCl. The resulting product was filtered and washed with 0.1 M acid and dried under dynamic vacuum for 24 h. The electrical conductivities ( $\sigma$ ) of the samples were measured using the standard four-probe or two-probe techniques on compressed thin pellets.

XPS measurements were carried out on a VG ESCALAB MkII spectrometer with a MgK $\alpha$  x-ray source (1253.5 eV photons). The powder samples were mounted on the sample studs with double-sided adhesive tape. The x-ray power supply was run at 12 kV and 10 mA, and the pressure in the analysis chamber during the scans was approximately 10<sup>-8</sup> mbar or less. All core-level spectra were referenced to the C1s neutral carbon peak at 284.6 eV and were curve-fitted with Gaussian component peaks. During deconvolution, the peak width (full width at half maximum or fwhm) was maintained constant for all components in a particular spectrum. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors and may be subject to  $\pm 10\%$  error. Since the surface compositions for all of the samples studied agreed fairly well with the bulk compositions obtained from chemical analysis, the present XPS results should be representative of the bulk properties.

## RESULTS AND DISCUSSION

### Polymer Composition and Conductivity

The elemental analysis of the homopolymers, poly(chloroaniline) and poly(iodoaniline), indicates that the halogen substituent/N ratio remains close to unity, unlike the poly(chloroaniline) obtained from electrochemical polymerization where as much as 40% of the halogen has been reported to be eliminated upon polymerization [7]. Thus, in the present work it

can be assumed that there is no halogen elimination upon polymerization of the substituted anilines, and the fraction of substituted aniline in the copolymer ( $F_1$ ) will be equal to the Cl/N or I/N ratio of the copolymer. The halogen/N ratios of the chloroaniline–aniline (CA) and iodoaniline–aniline (IA) copolymers as determined by XPS are compared with the mole fraction of substituted aniline in the initial monomer feed in Table 1. In this table the copolymers CA1 to CA4 and IA1 to IA4 were synthesized in  $H_2SO_4$  while IA5 and IA6 were synthesized in HCl. These results show that the fraction of substituted aniline in the product is close to or slightly higher than the fraction in the monomer feed. Hence, the presence of the Cl or I substituted group in the ortho-position does not adversely affect the polymerization process. However, the electrical conductivity ( $\sigma$ ) of the copolymer is strongly affected by the fraction of substituted aniline in the copolymer (Table 1). For polyaniline synthesized in HCl or  $H_2SO_4$ ,  $\sigma$  is 2–3 S/cm. However,  $\sigma$  of the CA or IA copolymer with about 50% substituted aniline units has decreased by a factor of  $\sim 50$  or  $10^4$ , respectively. In polyaniline, it has been shown that  $\sigma$  is a strong function of the protonation or “doping” level [3]. Thus, the protonation level of the copolymers will be discussed in the following sections.

### Structure of $H_2SO_4$ Protonated Samples

The N1s XPS core-level spectra of the copolymers and homopolymers are skewed toward the high binding energy (B.E.) side. The high binding energy component can be assigned to positively charged nitrogen [5, 8]. This high binding energy tail is much less prominent in the substituted aniline polymers and in the copolymers with a high mole fraction of substituted aniline. This is illustrated in Fig. 1. In the deconvolution of the N1s spectra, the following peak assignments are made: imine peak at 398.1 eV, amine peak at 399.3 eV, and positively charged nitrogen at B.E.  $> 401$  eV. The justification of the peak assignments was discussed in a previous publication [10]. The distribution of the imine, amine, and positively charged nitrogen in the copolymers and homopolymers synthesized in  $H_2SO_4$  is tabulated in Table 2. The degree of protonation is given by the  $N^+/N$  ratio, and in the idealized case of “acid doping” of polyaniline with protonation occurring at every imine unit, the  $N^+/N$  ratio is expected to be 0.5 [3]. For polyaniline synthesized in  $H_2SO_4$  and the CA and IA copolymers of low  $F_1$  ( $< 0.5$ ) which are also synthesized in  $H_2SO_4$ , the  $N^+/N$  ratio is fairly close to the ideal value, and the amount of

TABLE 1. Halogen/N Ratio and Electrical Conductivity ( $\sigma$ ) of Halogen-Substituted Aniline-Aniline Copolymers

Sample	Monomer system	Polymerization medium	Mole fraction of substituted aniline in monomer feed	XPS surface stoichiometry		$\sigma$ , S/cm
				Cl/N	I/N	
CA1	Aniline/2-chloroaniline	H <sub>2</sub> SO <sub>4</sub>	0.17	—	0.17	1
CA2	Aniline/2-chloroaniline	H <sub>2</sub> SO <sub>4</sub>	0.33	—	0.29	$6 \times 10^{-1}$
CA3	Aniline/2-chloroaniline	H <sub>2</sub> SO <sub>4</sub>	0.50	—	0.51	$5 \times 10^{-2}$
CA4	Aniline/2-chloroaniline	H <sub>2</sub> SO <sub>4</sub>	0.67	—	0.70	$2 \times 10^{-3}$
IA1	Aniline/2-iodoaniline	H <sub>2</sub> SO <sub>4</sub>	0.17	0.21	—	$10^{-1}$
IA2	Aniline/2-iodoaniline	H <sub>2</sub> SO <sub>4</sub>	0.33	0.39	—	$5 \times 10^{-3}$
IA3	Aniline/2-iodoaniline	H <sub>2</sub> SO <sub>4</sub>	0.50	0.58	—	$10^{-4}$
IA4	Aniline/2-iodoaniline	H <sub>2</sub> SO <sub>4</sub>	0.67	0.71	—	$5 \times 10^{-6}$
IA5	Aniline/2-iodoaniline	HCl	0.17	0.20	0.26	$4 \times 10^{-2}$
IA6	Aniline/2-iodoaniline	HCl	0.50	0.60	0.19	$2 \times 10^{-4}$

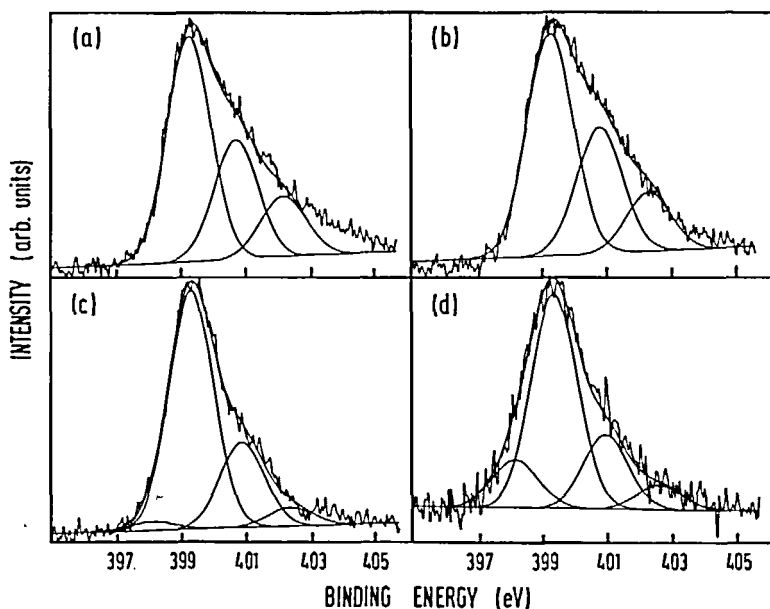


FIG. 1. N1s XPS core-level spectra of (a) polyaniline, (b) chloroaniline-aniline copolymer of  $F_1 = 0.17$ , (c) chloroaniline-aniline copolymer of  $F_1 = 0.70$ , and (d) poly(chloroaniline). All four samples were synthesized in  $H_2SO_4$ .

nitrogen existing as imine units is insignificant. However, as  $F_1$  increases beyond 0.5, the  $N^+/N$  ratio decreases, and for poly(chloroaniline) and poly(iodoaniline), about 14 and 17%, respectively, of the nitrogen remains as unprotonated imine units. A comparison of the  $N^+/N$  ratios for the CA and IA copolymers also indicates that the protonation is slightly less effective with the iodine substituent present at the ortho-position of the ring. It is interesting to note that although the  $N^+/N$  ratios of CA1, CA2, CA3, IA1, IA2, and polyaniline are quite similar, the  $\sigma$ 's of these samples are substantially different from one another. Thus, the electrical conductivity is affected not only by the protonation level but also by the presence of a substituent group on the ring.

The S2p XPS core-level spectra of the copolymers (Samples CA1 to CA4, IA1 to IA4) and homopolymers synthesized in  $H_2SO_4$  show the presence of a single species with a S2p<sub>3/2</sub> B.E. of 168.6 eV, consistent with

TABLE 2. Protonation Level of Polyaniline, Poly(Chloroaniline), Poly(Iodoaniline), and Copolymers Synthesized in  $H_2SO_4$ 

Sample	XPS surface stoichiometry			
	S/N	=N-/N	-NH-/N	N <sup>+</sup> /N
Polyaniline	0.52	0.0	0.55	0.45
CA1	0.54	0.0	0.55	0.45
CA2	0.57	0.0	0.58	0.42
CA3	0.52	0.03	0.57	0.40
CA4	0.34	0.03	0.68	0.29
Poly(chloroaniline)	0.29	0.14	0.60	0.26
IA1	0.47	0.01	0.60	0.39
IA2	0.46	0.0	0.61	0.39
IA3	0.28	0.06	0.73	0.21
IA4	0.32	0.14	0.68	0.18
Poly(iodoaniline)	0.20	0.17	0.56	0.27

a sulfate environment [11]. However, the valency of the sulfate anion associated with the nitrogenium cation needs to be resolved. In electrochemically prepared  $H_2SO_4$  samples, the presence of  $SO_4^{2-}$  and  $HSO_4^-$  anion species were considered but not resolved [8]. In the present work, the S/N and N<sup>+</sup>/N ratios are compared in Table 2. In general, the S/N ratio is close to or slightly higher than the N<sup>+</sup>/N ratio. Hence, to maintain charge neutrality, each sulfate group is only associated with a unit charge, and the anion species in  $H_2SO_4$  protonated polyaniline, poly(substituted aniline)s, and their copolymers is probably in the form of  $HSO_4^-$  monovalent anion. The slightly high S/N ratio may be attributed to the presence of  $H_2SO_4$  from the synthesis step since  $H_2SO_4$  is a nonvolatile acid and is not removed in the pumping process [2].

Additional information on the structure of the copolymers may be



obtained from the IR absorption spectra. The IR absorption spectra of ortho-substituted aniline homopolymers show bands at 1030, 880, 810, and 750  $\text{cm}^{-1}$ , suggesting the presence of 1,2,4 and 1,2 ring substitution [12]. The 1,2,4 substitution pattern would be consistent with the polymerization of ortho-substituted aniline units occurring at the para-position. One possible explanation for the presence of 1,2 substitution is the occurrence of short chains in the poly(substituted aniline)s and hence the terminal units contribute to this substitution pattern. The relatively high solubility of the poly(substituted aniline)s in organic solvents is consistent with a structure of fairly short chains. The linking of the ortho-substituted anilines in the ortho-position has been ruled out since elemental analysis of these polymers show a halogen/N ratio close to unity. In the copolymers, as the fraction of substituted aniline,  $F_1$ , decreases, the 810  $\text{cm}^{-1}$  band grows relative to the 880  $\text{cm}^{-1}$  band, suggesting a predominance of 1,4 substitution [12].

### Structure of HCl Protonated Samples

The  $\text{Cl}2p$  core-level spectra for the IA copolymers (Samples IA5 and IA6) and polyaniline synthesized in HCl can be fitted with  $\text{Cl}2p_{1/2}$  and  $\text{Cl}2p_{3/2}$  components at B.E. positions corresponding to those for covalent and ionic chlorine species (Fig. 2a, b, c). The  $\text{Cl}2p_{3/2}$  B.E. corresponding to these two species are at 200.2 and 197.2 eV, respectively. The presence of chlorine with covalent character has been widely observed in protonated polyaniline and related model compounds [4, 13]. However, as can be seen from Fig. 2, the proportions of the two chlorine species in polyaniline and copolymers are vastly different. In polyaniline the ratio of ionic chlorine to covalent chlorine ( $\text{Cl}^-/\text{—Cl}$ ) is 2.6 : 1 whereas this ratio has decreased to 1.1 : 1 in IA6 which has 60% substituted aniline units. The ratio of total chlorine to nitrogen ( $\text{Cl}/\text{N}$ ) also decreases as the fraction of iodoaniline in the copolymer increases to 0.60 (Table 3). However, for poly(iodoaniline), the  $\text{Cl}/\text{N}$  ratio is higher than the copolymers, but 89% of the chlorine incorporated is covalently bonded. Moreover, the negative B.E. shift ( $\sim 1.8$  eV) for the remaining 11% of the chlorine is substantially lower than the shift of 3 eV observed for a true ionic chloride species. (Compare Fig. 2a and Fig. 2d.)

The N1s XPS core-level spectra of the copolymers and homopolymers synthesized in HCl also show a high binding energy tail. Using the previously mentioned technique for the deconvolution of these spectra, the

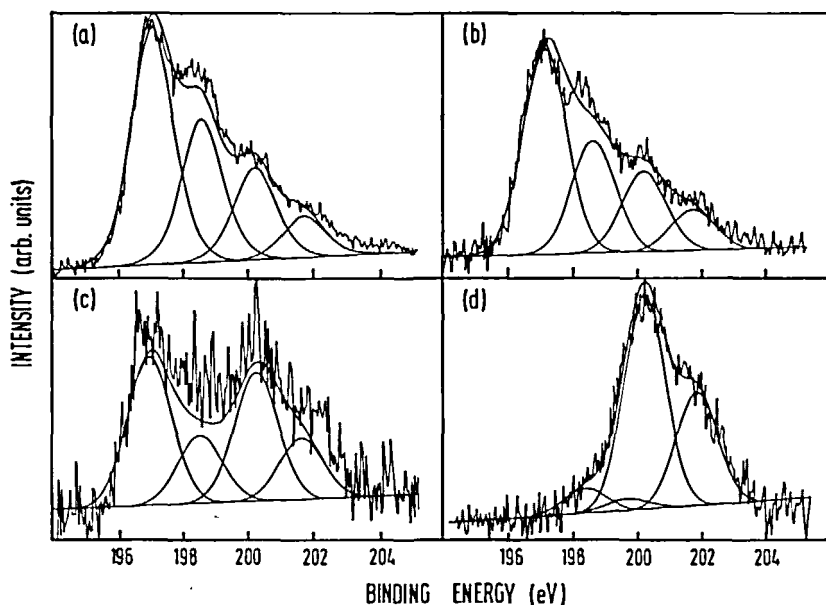


FIG. 2. Cl<sub>2</sub>p XPS core-level spectra of (a) polyaniline, (b) iodoaniline-aniline copolymer of  $F_1 = 0.20$ , (c) iodoaniline-aniline copolymer of  $F_1 = 0.60$ , and (d) poly(iodoaniline). All four samples were synthesized in HCl.

proportions of imine, amine, and positively charged nitrogen can be obtained and are tabulated in Table 3. As expected, the  $N^+/N$  ratio is less than the  $Cl/N$  ratio since some of the chlorine is covalently bonded. However, the  $N^+/N$  ratio agrees quite well with the  $Cl^-/N$  ratio. In samples of low degrees of protonation, the possibility of surface oxidation may contribute significantly to the  $N^+/N$  ratio. This contribution has been observed even in totally deprotonated samples (see next section).

A comparison of the protonation levels in samples synthesized in  $H_2SO_4$  (Table 2) with that of samples synthesized in HCl (Table 3) indicates that  $H_2SO_4$  is more effective as a protonating agent for both the homopolymers and the copolymers. For samples synthesized in HCl, a portion of the nitrogen remains unprotonated as imine units, and the proportion of imine increases as the amount of substituted aniline units in the copolymer sample increases.

TABLE 3. Protonation Level of Polyaniline, Poly(Iodoaniline), and Copolymers Synthesized in HCl

Sample	XPS surface stoichiometry					
	Cl/N	Cl <sup>-</sup> /N	-Cl/N	=N-/N	-NH-/N	N*/N
Polyaniline	0.51	0.37	0.14	0.06	0.64	0.30
IA5	0.26	0.19	0.07	0.06	0.71	0.23
IA6	0.19	0.10	0.09	0.09	0.73	0.18
Poly(iodoaniline)	0.35	0.04 <sup>a</sup>	0.31	0.21	0.70	0.09

<sup>a</sup>This amount of chlorine may not be truly ionic since its B.E. is at 198.4 eV.

**Structural Changes with Base, Chloroform, and Heat Treatment**

Treatment of the homopolymers and copolymers with excess 0.5 M NaOH converts these polymers to the base form with complete elimination of S and Cl<sup>-</sup> from the samples synthesized in H<sub>2</sub>SO<sub>4</sub> and HCl, respectively. The N1s core-level spectra of these polymers in the base form can be deconvoluted by using the method described earlier [10] to yield the intrinsic oxidation state, i.e., the proportion of imine and amine units. The N1s core-level spectra of deprotonated polyaniline and poly(chloroaniline) synthesized in H<sub>2</sub>SO<sub>4</sub> are compared in Fig. 3. The proportions of nitrogen existing as imine and amine units are 41 and 48%,

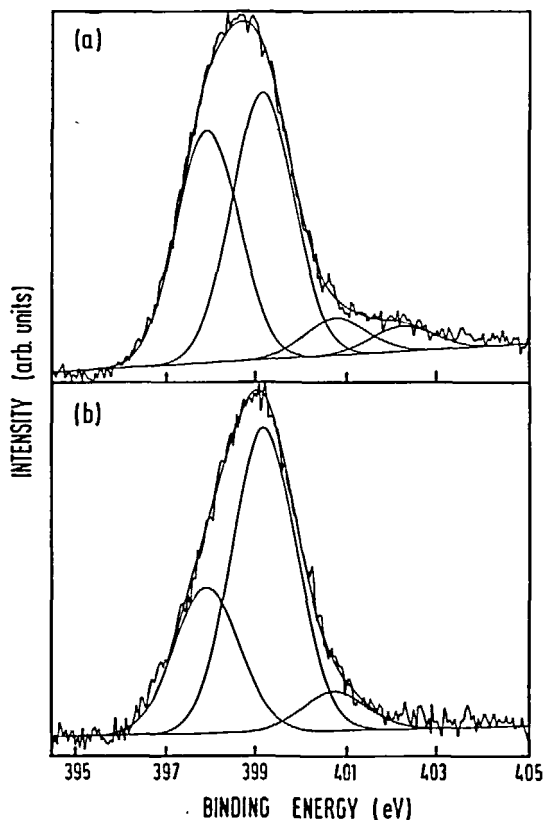


FIG. 3. N1s XPS core-level spectra of (a) deprotonated polyaniline and (b) deprotonated poly(chloroaniline).

respectively, in polyaniline, but the corresponding values for poly(chloroaniline) are 30 and 62%, respectively. The imine : amine ratios of the CA copolymers are closer to 1 : 2 as in poly(chloroaniline) than to the ratio in polyaniline. The decrease in the intrinsic oxidation state of the polymer caused by the ring substituent is also apparent from the N1s core-level spectra of the IA copolymers and poly(iodoaniline) samples synthesized in either  $H_2SO_4$  or HCl. In most of the present base polymers, there is a residual high B.E. tail indicating that about 10% of the nitrogen is positively charged and is probably related to surface oxidation. The presence of surface oxidation has also been reported in other XPS studies of polyanilines [13].

The unsubstituted aniline polymers synthesized in either HCl or  $H_2SO_4$  show negligible solubility in chloroform, and the electrical conductivity is also not significantly altered after chloroform treatment. In contrast, poly(chloroaniline) and poly(iodoaniline) synthesized in  $H_2SO_4$  show partial solubility while poly(iodoaniline) synthesized in HCl is almost completely soluble in chloroform. This suggests that the substituted aniline polymers consist of fairly short chains. The CA copolymers show partial solubility in chloroform but the solubility is less than that of the IA copolymers with similar  $F_1$ 's even though poly(chloroaniline) and poly(iodoaniline) synthesized in  $H_2SO_4$  have quite similar solubilities. The chemical composition of the insoluble fraction after  $CHCl_3$  treatment is not drastically different from those of the original samples. The halogen substituent/N ratio of the chloroform insoluble fraction of copolymers and substituted aniline polymers are about 0.8 to 0.95 of the values of the pristine samples. This suggests that the composition of the polymer chains is fairly uniform regardless of chain length. The ratio of protonating acid species to N (S/N or Cl/N) of the chloroform insoluble fraction of the copolymers is about 20% to 30% higher than that of the pristine sample. It is possible that the insoluble fraction consists of longer chains with a higher imine : amine ratio in the intrinsic oxidation state and have a slightly higher degree of incorporation of the acid species. However, the electrical conductivity of the insoluble fraction is not significantly different from that of the pristine sample.

The electrical conductivity of the copolymers decreases after heat treatment in air at  $150^\circ C$  for 2 h. It appears that the predominant factor determining the extent of decrease in  $\sigma$  upon heat treatment is the protonating acid species rather than the halogen substituent in the ring. The  $\sigma$  of CA1 and IA1 copolymers which are synthesized in  $H_2SO_4$  decreases by a factor of 3, while  $\sigma$  of IA5 copolymer which is synthesized

in HCl decreases by a factor of 50. The three copolymers have similar proportions of substituted aniline units, and the proportions are 0.17, 0.21, and 0.20 for CA1, IA1, and IA5, respectively. A comparison of the XPS surface stoichiometries of the samples before and after heat treatment indicate that the ratio of the protonating acid species to total N (S/N for CA1 and IA1, Cl/N for IA5) does not change significant upon heat treatment. However, the fraction of chlorine that is ionic has decreased from 0.72 to 0.46, indicating a conversion of ionic chlorine to covalently bonded species. The conversion of ionic chlorine to covalently bonded species upon heat treatment has also been reported in other studies on polyaniline [14, 15]. The nature of S in CA1 and IA1, however, does not appear to be altered by the heat treatment.

### CONCLUSION

The chemical polymerization of 2-chloroaniline and 2-iodoaniline, and the copolymerization of these substituted anilines with aniline proceed without elimination of the substituent group, and the units are probably joined at the para-position. The protonation level of the copolymers synthesized in  $H_2SO_4$  as indicated by the  $N^+/N$  ratio is approximately constant at 0.4 to 0.5 for copolymers with the substituted aniline fraction of less than 0.5, but decreases appreciably at higher substituted aniline fractions. The electrical conductivity is more adversely affected by the presence of the substituent group and decreases significantly even when the fraction of substituted aniline units is 0.5 or less. A higher degree of protonation is achieved when  $H_2SO_4$  rather than HCl is used as the protonating acid species. In the former case the sulfate species is probably the  $HSO_4^-$  monovalent anion. When HCl is used, a significant fraction of the chlorine incorporated is covalently bonded with the polymer and a portion of the imine nitrogen remains unprotonated. The imine/amine ratio in the base state of the copolymers and poly(substituted aniline)s is also lower than that of polyaniline. The copolymers also show partial solubility in chloroform, and the electrical conductivity of the chloroform-treated samples is not changed from the value prior to treatment.

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