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K. G. Neoh[a]; K. L. Tan[b]; T. C. Tan[a]; E. T. Kang[a]
[a] Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore [b] Department of Physics, National University of Singapore, Kent Ridge, Singapore

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EFFECTS OF PROTONIC ACIDS ON POLYANILINE STRUCTURE AND CHARACTERISTICS

K. G. NEOH

Department of Chemical Engineering

K. L. TAN

Department of Physics

T. C. TAN and E. T. KANG

Department of Chemical Engineering

National University of Singapore
Kent Ridge, Singapore 0511

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ABSTRACT

Chemical polymerization of aniline in five different protonic acids, HCl, H_2SO_4, HBr, HNO_3, and acetic acid (HAc), has been studied. The resulting polymers are characterized by elemental analysis, thermogravimetric analysis, infrared and x-ray photoelectron spectroscopy, and electrical conductivity measurements. It is found that a large fraction of the bromine and a smaller fraction of the chlorine in the product is covalently bonded. Thus a more accurate indicator of the degree of protonation would be the halogen anion rather than total halogen content. When H_2SO_4 is used for protonation, the anion incorporated in the polyaniline appears to be the HSO_4^- rather than the SO_4^{2-} species. The degree of protonation of H_2SO_4 protonated polyaniline is significantly reduced when it is washed with water after the synthesis step. Treatment of the H_2SO_4, HBr, and HNO_3 protonated polyaniline with HCl results in almost complete replacement of the respective anion by the chloride anion. The HBr protonated polyaniline sample shows partial solubility in $CHCl_3$, with the insoluble fraction showing a slight improvement in conductivity after $CHCl_3$ treatment.

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INTRODUCTION

Conducting polyaniline is usually obtained by the oxidative polymerization of aniline in HCl by $(NH_4)_2S_2O_8$ to yield emeraldine hydrochloride (PAn-HCl) [1]. The emeraldine hydrochloride can be treated with NH_4OH to yield the insulating state, emeraldine base, which consists of equal numbers of reduced $[-(C_6H_4)-(NH)-(C_6H_4)-(NH)-]$ and oxidized $[-(C_6H_4)-N=(C_6H_4)=N-]$ repeat units [1]. Protonation of the emeraldine base by HCl converts it back to PAn-HCl with the protonation occurring preferably at the imine nitrogen [2]. From x-ray photoelectron spectroscopy (XPS), the chlorine incorporated has been observed to exist as both chloride anions and covalently bonded chlorine [3].

The structure and characteristics of PAn-HCl have been extensively investigated and reported, but a systemic comparison of the interaction of polyaniline with other protonic acids is lacking. In the electrochemical polymerization of aniline, it has been reported that different synthesis media can induce differences in the polyaniline [4, 5]. Polyaniline, which is soluble in common organic solvents, can be synthesized by using organic protonic acids of large molecular size, and it has been suggested the solubility is due to reduced interchain interactions because of the large size of the counteranion [6]. The chemical polymerization of aniline with different oxidizing agents [7] and with different oxidant/monomer ratios [8] in HCl has recently been explored. In this work we synthesized protonated polyaniline in HCl, HBr, H_2SO_4, HNO_3, and HAc (acetic acid). The physicochemical properties of the resulting emeraldine salts are investigated with a variety of experimental techniques and compared in order to obtain a better understanding of the interaction of the different "doping" acids with the polyaniline.

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EXPERIMENTAL

The emeraldine salt was synthesized by the oxidative polymerization of aniline by $(NH_4)_2S_2O_8$ in the appropriate acid. The five acids used were HCl, HBr, H_2SO_4, HNO_3, and HAc (acetic acid), and the acid concentration used was 1.2 *M*. The resulting product was filtered, washed with deionized water, and dried under dynamic vacuum for 30 h. For comparison purposes, some HCl and H_2SO_4 protonated polyaniline samples were washed with 0.1 *M* acid instead of water. The resultant emeraldine salts were characterized by a variety of experimental techniques. The chemical composition determination and structural analysis were carried out with elemental analysis, infrared (IR) absorption spectroscopy, and x-ray photoelectron spectroscopy (XPS). The latter was conducted with a ESCALAB MkII spectrometer with a MgK_α x-ray source (1253.6 eV). The powdery samples were mounted on standard sample studs with double-sided adhesive tape. All spectra were referenced to the C1s

peak at 284.6 eV, and the peak areas were corrected using experimentally determined sensitivity factors. IR absorption spectroscopy was carried out by using a Perkin-Elmer 682 spectrophotometer with the samples dispersed in KBr.

The electrical conductivity (σ) of the samples was measured by compressing the powdery samples into pellets and using the standard collinear four-probe method. The thermal stability of the samples in N_2 was determined gravimetrically with a Netzsch STA409 simultaneous thermogravimetric-differential thermal analyzer. The effect of heating on σ was assessed by maintaining the sample at 150°C in air for 2 h. The ability of the samples to sustain a high current density was tested by passing a fixed current through the pellet and measuring the voltage drop across it. A constant dc power source (Hewlett-Packard Model 6212B) was used to maintain a steady current even if the conductivity of the sample changed. A Keithley 614 electrometer connected to a strip chart recorder was used to monitor the voltage continuously.

The samples were also dispersed in chloroform and aqueous HCl for 24 h at room temperature. After the treatment period, the weight change and σ were measured, and IR absorption spectroscopy and XPS were carried out to elucidate the effects of the two solutions on the samples.

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RESULTS AND DISCUSSION

Chemical Composition and Spectroscopy Results

The chemical composition of the protonated polyaniline samples, which will be denoted generically as PAn-HX in the following discussion, as determined by elemental analysis (with oxygen determined by difference), is given in Table 1. These

TABLE 1. Chemical Composition of Protonated Polyaniline Samples

Sample	Chemical composition (bulk)	XPS surface stoichiometry[a]		
		X/N	X^-/N	-X/N
PAn-H_2SO_4	$(C_{24.0}H_{21.0}N_{3.89})(HSO_4)_{1.13}$	0.31	0.31	—
PAn-HBr	$(C_{24.0}H_{18.6}N_{3.86})(Br)_{3.41}$	0.89	0.32	0.57
PAn-HNO_3	$(C_{24.0}H_{19.8}N_{4.0})(NO_3)_{0.57}$	0.15	0.15	—
PAn-HAc	$(C_{24.0}H_{20.3}N_{4.0})(CH_3COO)_{0.33}$	—	—	—

[a]Based on N1s and respective species (X, X^-, or –X) spectral areas after correcting with experimentally determined sensitivity factors.

results are for the water-washed samples. Theoretically, the composition of PAn-HX can be formulated as $(C_{24}H_{18}N_4)(HX)_n$. For emeraldine hydrochloride, the chemical composition determined experimentally has been reported to be $(C_{24}H_{18}N_4)(HCl)_2(H_2O)_{2.3}$ [7]. In the present work the excess hydrogen may also be due to H_2O molecules which have been reported to be bound to the polymer, probably via hydrogen bonding with the existing protons [7, 9]. The excess oxygen (after accounting for that present in the acidic anion) amounts to about 10% of the sample weight. Excess oxygen has also been reported for both chemically [7] and electrochemically [10] synthesized PAn-HCl. Although a portion of this oxygen is probably due to bound water, it is possible that there are other as yet undetermined species with which the oxygen is associated.

The formulation of PAn-HX as $(C_{24}H_{18}N_4)(HX)_n$ can be misleading since it gives no information as to the fraction of X that may be covalently bonded and hence not available as anions. In our earlier investigations on PAn-HCl, we reported XPS data which showed that although the total chlorine-to-nitrogen ratio (Cl/N) is close to 0.5, about 1/4 of the total chlorine is of a covalent nature [11, 12]. Similar XPS measurements were carried out with the PAn-H_2SO_4, PAn-HBr, and PAn-HNO_3 samples. The S2p core-level spectrum of the PAn-H_2SO_4 sample shows a peak at 168.6 eV, consistent with a sulfate environment [13]. The presence of NO_3^- anions in the PAn-HNO_3 sample is indicated by a peak at approximately 406 eV in the N1s core-level spectrum. The Br3d spectrum of the PAn-HBr sample indicates the presence of two different types of bromine. This is illustrated in Fig. 1(a). The ionic component is at 68 eV while the component at about 70.5 eV is attributable to the covalently bonded bromine. It is obvious that a larger fraction of the bromine exists as covalently bonded species. From the XPS data the ratios total bromine/N, bromide anion/N, and covalently bonded bromine/N (Br/N, Br^-/N, and –Br/N, respectively) are calculated, and these are given in Table 1 together with the sulfate/N and nitrate/N ratios. The sulfate/N, Br/N, and nitrate/N ratios as calculated from XPS peak area ratios agree well with those calculated from elemental analysis.

The use of a divalent acid such as H_2SO_4 for protonation of PAn gives rise to ambiguity as to the identity of the anion, i.e., the SO_4^{2-} or HSO_4^- anion. Since the number of positive and negative charges has to be equal to maintain charge neutrality in the sample, the valency of the anion can be obtained by comparing the S/N and N^+/N ratios. The N1s spectrum of protonated polyaniline are skewed toward the high binding energy side. The high binding energy component can be assigned to positively charged nitrogen [10, 14]. The N1s spectrum of the PAn-H_2SO_4 sample is shown in Figure 1(b). In the deconvolution of the N1s spectrum, the following peak assignments are made: imine peak at 398.1 eV, amine peak at 399.3 eV, and positively charged nitrogen at >401 eV. The justification of the peak assignments was discussed in a previous publication [11]. The N^+/N ratio obtained from the XPS

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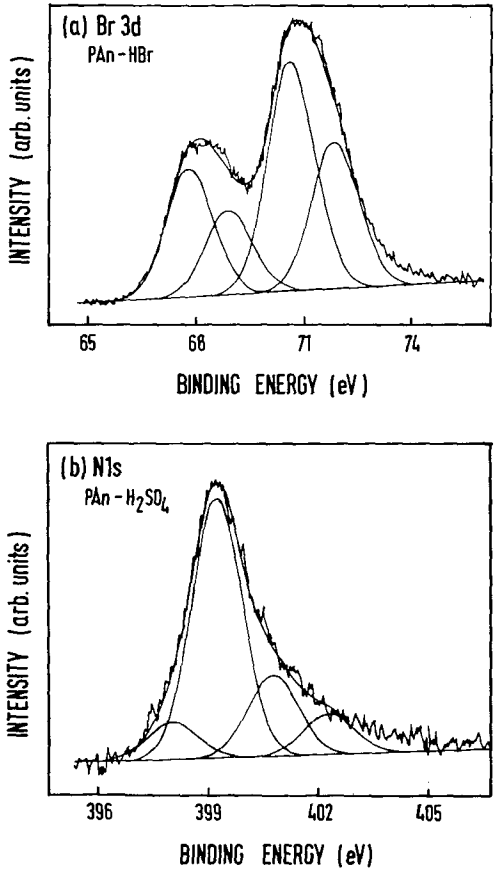

FIG. 1. XPS core-level spectra: (a) PAn-HBr, Br3d; (b) PAn-H_2SO_4, N1s.

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measurements of the PAn-H_2SO_4 sample is 0.29, while the S/N ratio is 0.31. Hence, to maintain charge neutrality, sulfur has to exist as monovalent anions, and HSO_4^- is thus the probable species.

The S2p core-level spectrum of the acid-washed PAn-H_2SO_4 also shows a single sulfate environment at 168.6 eV. However, the S/N ratio is calculated to be 0.52, which is significantly higher than the value obtained with the water-washed sample. The N1s core-level spectrum of the acid-washed sample correspondingly shows a much more prominent high binding energy tail, and the N^+/N ratio is calculated to be 0.45. For PAn-HCl, the Cl^-/N and Cl/N ratios of the acid-washed sample show only a small increase over the water-washed sample.

Electrical and Thermal Properties

The electrical conductivity (σ) of the water-washed PAn-HCl and PAn-H_2SO_4samples is about 2 and 0.7 S/cm, respectively. For PAn-HBr, PAn-HNO_3, and PAn-HAc, σ is 0.3, 0.5, and 0.2, respectively. Although the degree of protonation (as indicated by X^-/N) of PAn-HBr is similar ot that of PAn-H_2SO_4 and PAn-HCl, its conductivity is lower. One possible reason is the large extent of covalent bond formation between PAn and bromine which disrupts the conjugation of the polymer. The σ of the acid-washed PAn-H_2SO_4 is about 4 times higher than that of the water-washed sample, but the σ of the acid-washed PAn-HCl does not differ significantly from that of the water-washed PAn-HCl sample. This is consistent with the XPS data discussed earlier. The ability of the polymer to sustain a high current density also depends on the acid used. The current-carrying capacity of PAn-HCl was reported in detail earlier [12]. As in the case of PAn-HCl, the PAn-H_2SO_4 and PAn-HBr samples can sustain a current density of 2 A/cm^2 over a 24-h period with no adverse effect. However, at higher current densities, these two samples break down at a faster rate than PAn-HCl. The PAn-HNO_3 and PAn-HAc samples are inferior to either PAn-H_2SO_4 or PAn-HBr.

The degree of degradation in σ upon heating is also dependent on the acid anion incorporated in the polyaniline. The ratio of the conductivity measured after 2 h at 150°C to that prior to heat treatment (σ_0) is given in the second column of Table 2. The decrease in σ is partially reversible, and a constant σ is obtained after leaving the sample for 24 h at room temperature and ~70% relative humidity (third column in Table 2). For PAn-HCl it has been shown that humidity plays an important role in the recovery of the conductivity of a heated sample. For this sample it has been postulated that the decrease in σ upon heating at 150°C is due to the loss of water associated with the polymer as well as the conversion of ionic chloride to the covalent species [12]. Water vapor is also found to affect σ of the other PAn-HX samples. A similar conversion of ionic bromide to covalent bromine is also clearly evident when the XPS data of the heated PAn-HBr sample is compared with that of the sample prior to heat treatment. However, the PAn-HBr sample shows a lower degree of degrada-

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TABLE 2. Effect of Temperature on Conductivity

	σ/σ_0	
Sample	2 h at 150°C	24 h after heat treatment
PAn-HCl	0.054	0.22
PAn-H_2SO_4	0.011	0.05
PAn-HBr	0.20	0.76
PAn-HNO_3	0.053	0.25

tion in σ upon heating than the PAn-H_2SO_4 and PAn-HNO_3 samples, and its σ subsequently recovers to a higher level than the latter two samples. The PAn-H_2SO_4 and PAn-HNO_3 samples do not show as substantial a decline in their anion/N ratio upon heating as either the PAn-HCl or PAn-HBr sample. Thus, the former two samples may have undergone other forms of structural changes upon heating which resulted in loss of conductivity.

The thermogravimetric (TG) scans of the PAn-HX samples in N_2 are shown in Fig. 2. With the exception of PAn-HBr, the samples generally show a small initial weight loss from 30 to 125°C followed by a plateau region and then a gradual weight loss step. The initial weight loss may be due to water and/or acid from the synthesis process. For the PAn-HCl, PAn-H_2SO_4, and PAn-HAc samples, after the initial weight loss there are no further weight changes until about 225°C, while the second weight loss step for PAn-HNO_3 commences about 50°C earlier. In the case of PAn-HBr, after the initial weight loss step, there is a sharp weight decline between 150 and 225°C followed by a more gradual weight loss. The relatively high rate of decomposition of PAn-HBr in the temperature range of 150 to 225°C is probably associated with bromine that is covalently bonded to PAn (see next section). Although it is not known at present whether the covalent bromine is due to ring substitution or the addition to the imine double bond or other sites, the formation of such bonds between PAn and bromine appears to weaken bonds within the polymer chain and/or interchain interactions resulting in increased thermal decomposition and solubility.

$CHCl_3$ and HCl Treatment

The weight and conductivity changes of the emeraldine salts after $CHCl_3$ treatment are shown in Table 3. (The subscript "0" denotes pristine sample.) The weight changes for the PAn-HCl, PAn-H_2SO_4, and PAn-HNO_3 samples are small, and the σ

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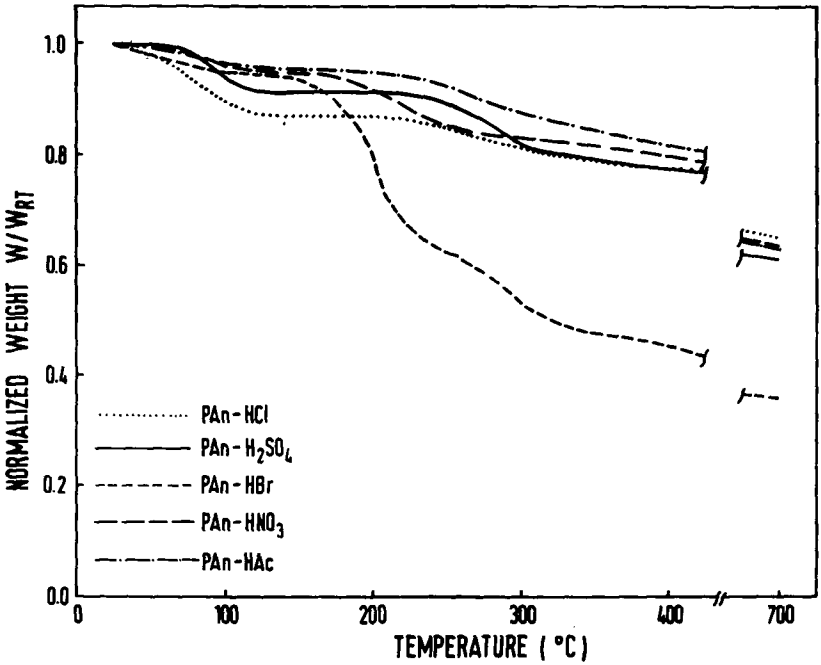

FIG. 2. Thermogravimetric scans of PAn-HCl, PAn-H_2SO_4, PAn-HBr, PAn-HNO_3, and PAn-HAc in N_2. W_{RT} is the weight at room temperature.

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TABLE 3. Effects of $CHCl_3$ Treatment

Sample	W/W_0	σ/σ_0	$[X^-/N]/[X^-/N]_0$[a]	$[-X/N]/[-X/N]_0$[a]
PAn-HCl	~1	0.8	0.91	1.1
PAn-H_2SO_4	0.98	0.9	1.0	—
PAn-HBr	0.56	2.0	0.93	0.47
PAn-HNO_3	0.97	1.4	0.98	—

[a]XPS surface stoichiometry based on N1s and respective species (X) spectral areas after correcting with experimentally determined sensitivity factors.

of these samples correspondingly shows minor changes. On the other hand, the PAn-HBr sample loses about 44% of its original weight but its σ shows a small increase. XPS analyses of the four samples before and after $CHCl_3$ treatment reveal no significant changes in the structure of the PAn-H_2SO_4 and PAn-HNO_3 samples. The acidic anion/N ratio for these two samples as calculated from the XPS spectral areas is similar before and after treatment (Table 3). For the PAn-HCl sample after $CHCl_3$ treatment, there is a small decrease in Cl^-/N and a small increase in –Cl/N, with the total Cl/N ratio remaining at approximately the same value as prior to $CHCl_3$ treatment. For the PAn-HBr sample, the Br content and nature are drastically affected by $CHCl_3$ treatment. Comparison of Br3d core-level spectra in Figs. 3(a) and 1(a) reveals that the fraction of bromine covalently bonded has decreased after $CHCl_3$ treatment. However, the Br^-/N ratio does not appear to be significantly affected by $CHCl_3$ (Table 3).

The UV-visible absorption spectrum of the PAn-HBr $CHCl_3$-soluble fraction is shown in Fig. 4. The $CHCl_3$-soluble fraction absorption spectrum shows strong bands at 240 and 310 nm followed by a weaker and broad band which peaks at about 520 nm. The bands in the UV region are associated with the ring structure while the broad band at 520 nm resembles that reported for aniline oligomers before proton acid doping [15]. Upon proton acid doping, this band has been reported to disappear [15]. Thus the $CHCl_3$-soluble fraction of PAn-HBr probably consists of aniline oligomers with the bromine being predominantly bonded covalently to the oligomer chains. On the other hand, the insoluble fraction after $CHCl_3$ treatment shows similarities with pristine PAn-HCl. The IR absorption spectrum of the former is shown in Fig. 5. The long absorption tail from 4000 to 1700 cm^{-1} and the intense and broad "electronic" band at 1130 cm^{-1}, which are characterisic of the protonated structure [16], remain prominent in the $CHCl_3$-treated sample. Other main absorption bands are located at 1580 and 1485 cm^{-1}, which are assigned to the quinone and benzoid ring stretching, respectively, at 1300 cm^{-1} and 1240 cm^{-1} due to C–N stretching of aromatic amines, and between 800 and 900 cm^{-1}, characteristic of aromatic bands of substituted rings [16]. In view of these similarities between the $CHCl_3$-treated PAn-HBr and pristine PAn-HCl, it is not surprising that the former sample should remain electrically conductive even after losing almost half of its original weight.

The removal of the $CHCl_3$-soluble fraction from pristine PAn-HBr not only increases the sample's conductivity but also its thermal stability. This is illustrated in Fig. 6. The TG scan of the $CHCl_3$-treated sample shows an initial weight loss from room temperature to 100°C followed by a plateau region and then a second weight loss step commencing at about 250°C. This trend is similar to that observed for the PAn-HCl, PAn-H_2SO_4, and PAn-HAc samples (Fig. 2). In contrast, the pristine PAn-HBr sample shows the major weight loss step commencing at 150°C. Hence, the presence of a substantial amount of covalently bonded bromine appears to decrease

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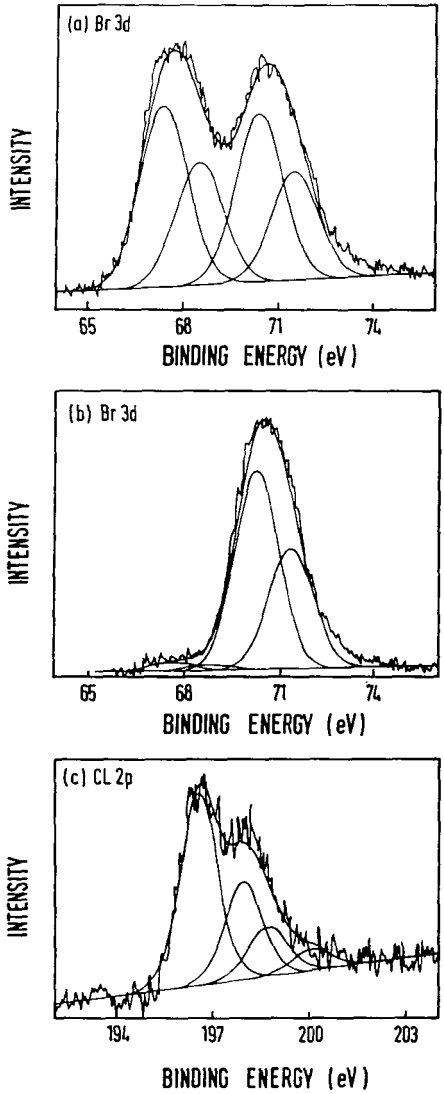

FIG. 3. XPS core-level spectra: (a) $CHCl_3$-treated PAn-HBr, Br3d; (b) HCl-treated PAn-HBr, Br3d; (c) HCl-treated PAn-HBr, Cl2p.

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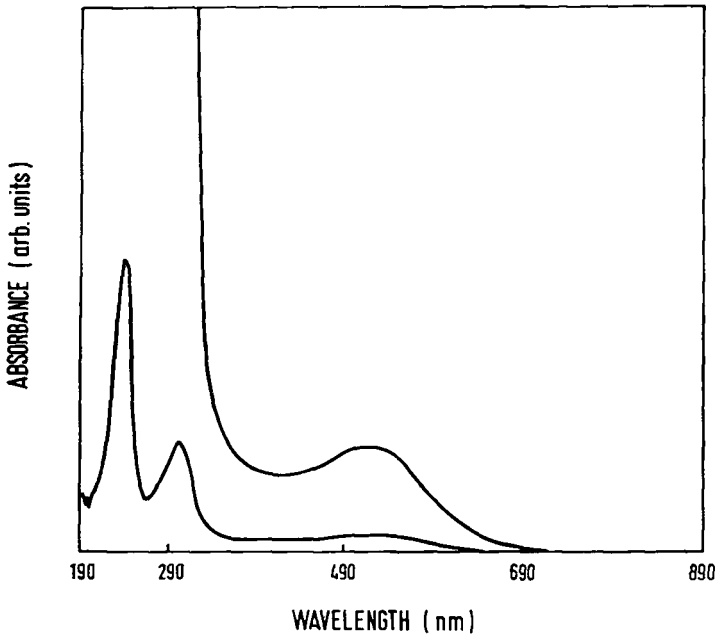

FIG. 4. UV-visible absorption spectrum of $CHCl_3$-soluble fraction of PAn-HBr.

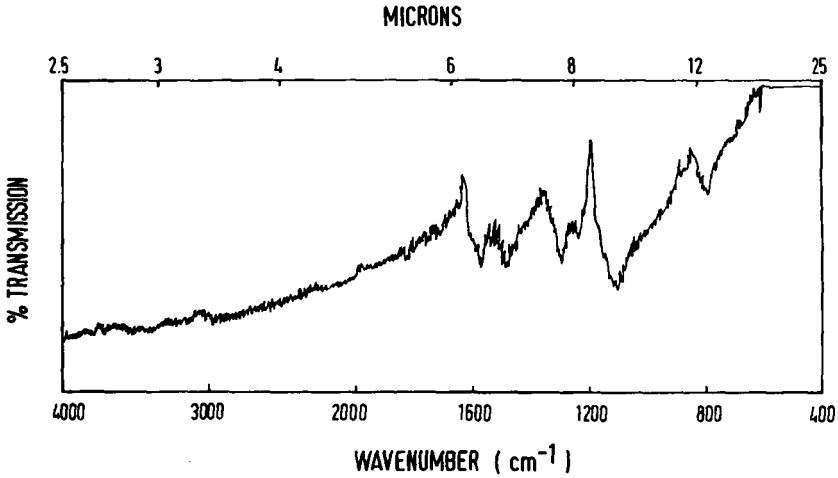

FIG. 5. IR absorption spectrum of $CHCl_3$-insoluble fraction of PAn-HBr.

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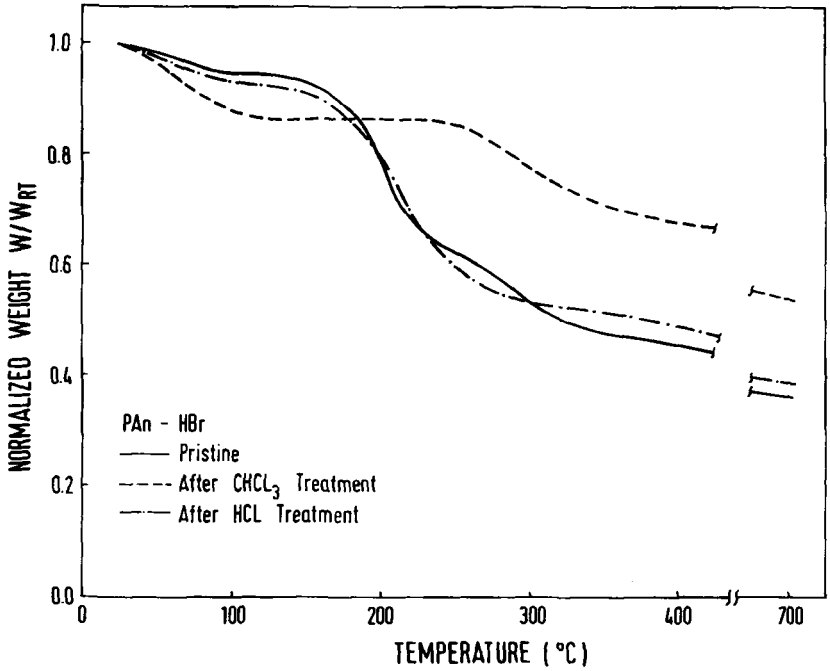

FIG. 6. Thermogravimetric scans of pristine, $CHCl_3$-treated, and HCl-treated PAn-HBr samples. W_{RT} is the weight at room temperature.

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the thermal stability of the polymer. This is further supported by the TG scan of the HCl-treated PAn-HBr sample. HCl treatment was found to remove the ionic bromide, but the covalent bromine was not significantly affected (see below). Thus it is not surprising that the TG scans of the HCl-treated and pristine PAn-HBr samples are so similar.

The most prominent result of HCl treatment of the PAn-HX samples is the almost complete replacement of the original anions in the respective samples by Cl^- anions. The exchange of anions is clearly evident from the XPS data of the samples after HCl treatment. This is illustrated in Fig. 3(b) and 3(c) which shows the Br3d and Cl2p spectra of the PAn-HBr sample after HCl treatment. The ionic bromide component at 68 eV has largely disappeared while the covalently bonded Br remains. The –Br/N ratio remains close to that prior to HCl treatment. The Cl2p spectrum shows a large ionic chloride component at 197 eV and a much smaller component at 200 eV, attributable to covalently bonded chlorine. The Cl^-/N and –Cl/N ratios do not vary

substantially for the three samples, PAn-H_2SO_4, PAn-HNO_3, and PAn-HAc, after HCl treatment. These ratios range from 0.28 to 0.30 and 0.06 to 0.09, respectively. However, the Cl^-/N ratio of 0.22 in the HCl-treated PAn-HBr sample is substantially lower, but the –Cl/N ratio of this complex is also about 0.06. These ratios are lower than the corresponding values of 0.36 and 0.15 in pristine PAn-HCl. Although chloride anions are incorporated into the samples during HCl treatment, the conductivity of these samples decreases by a factor of 5 or more. The decrease in σ may indicate that the HCl treatment has resulted in structural changes of the PAn-HX samples that are more complex than direct anion exchange.

CONCLUSION

In the chemical synthesis of polyaniline by ammonium persulfate, the acidic anion can play an important part in determining the physicochemical properties of the product. The degree of protonation as indicated by X^-/N rather than X/N is highest when HCl, HBr, and H_2SO_4 are used. XPS has shown that a large fraction of Br and a smaller fraction of Cl exists as covalently bonded species and hence would not have participated in the "doping" of the polymer. As a result of the substantial amount of covalent bromine in PAn-HBr, this emeraldine salt exhibits increased solubility in $CHCl_3$ and reduced thermal stability. When H_2SO_4 is used for protonation, the anion incorporated appears to be the HSO_4^- rather than the SO_4^{2-} species. On the basis of electrical conductivity, electrical, thermal, and chemical stability of the product, HCl and H_2SO_4 are the most suitable acids for use in the protonation of polyaniline.

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