Preparation and Characterization of Electrically Conducting Copolymers of Aniline and Anthranilic Acid: Evidence for Self-Doping by X-ray Photoelectron Spectroscopy

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ABSTRACT: Homopolymers and copolymers based on anthranilic acid and aniline have been chemically prepared and characterized by a number of techniques including X-ray photoelectron spectroscopy (XPS), thermogravimetry (TG), and differential scanning calorimetry (DSC). The solubility increases while the conductivity decreases with the amount of anthranilic acid in the system. XPS results indicate concurrent self-doping by the –COOH group. The degree of protonation remains at ≈20–30% but the conductivity varies drastically depending on the amount of self-doping versus external doping by HCl. DSC results suggest intramolecular and intermolecular interactions through hydrogen bonding made possible by the –COOH group. These and other results have been rationalized on the basis of the effect of the –COOH substituent on the polymer structure.

Introduction

Polyaniline (PAN) has been known in a variety of forms for over a century,[1,2] and as such must be considered as the oldest of the conducting polymers. It has always been at the forefront in the global search for commercially viable conducting polymers because of its unique reversible proton dopability, excellent redox recyclability, chemical stability, variable electrical conductivity (which can be "tuned" by varying the pH at which it is prepared), low cost, and ease of preparation. In view of this, PAN can be used as an electrode material,[3,4] in the fabrication of secondary batteries,[5–7] in microelectronics,[8,9] and as an electrochromic material.[10–12] Future high-technology applications in the area of recordable optical disks[13] and chemical sensors have also been suggested.[14]

The commerical exploitation of PAN has been hampered by its intractable nature, as it is normally produced as an insoluble powder chemically or as a thin brittle film electrochemically. In the last few years, however, considerable progress has been made in the processing of conducting polymers by, for example, preparation of polymer composites,[15,16]; preparation of soluble polymers,[17,18] and the use of plasma polymerization.[19] A brief review of the subject is given by Genies.[20] Recently, the postsulfonation of PAN yielded a soluble self-doping PAN with $\sigma \approx 0.1$ S cm^{-1}.[21] This approach is attractive as it eliminates the use of external dopants whose stabilities have always been a problem associated with many practical applications of the material. Poly(anthranilic acid) (PANA), another aniline-based polymer capable of self-doping, was prepared electrochemically, which had only a limited solubility and a low conductivity.[22] We would like to report in this article the chemical preparation and characterization of copolymers based on aniline and anthranilic acid with the aim to (i) improve the solubility compared with PAN, (ii) study the self-doping mechanism by XPS, and (iii) evaluate the thermal properties of the polymers.

Experimental Section

Chemicals. Aniline and anthranilic acid were purchased from Aldrich Chemicals Co. Inc. Sodium persulfate ($Na_2S_2O_8$) and hydrochloric acid (HCl) were obtained from BDH. The aniline was distilled and stored under nitrogen in the dark prior to polymerization. Anthranilic acid was recrystallized from H_2O; mp 145–147 °C.

Synthesis of Doped Polyaniline (PAN–HCl). A 50-mL solution of $Na_2S_2O_8$ (3.8 g, 16 mmol) was slowly added dropwise with constant stirring to a 100-mL solution containing fresh aniline (1.5 ml, 16 mmol) and about 1.0 M of HCl to maintain a pH of about 0.1. Polymerization was carried out at room temperature for about 24 h, after which the polymer powder formed was filtered, washed with a small amount of HCl, and dried in a desiccator containing phosphorus pentoxide (P_2O_5). The green powder obtained was insoluble in all solvents. The blue powder obtained by treating PAN–HCl with sodium hydroxide (NaOH) to form the base was soluble in *N*-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) to give deep blue solutions.

Synthesis of Doped Poly(anthranilic acid) (PANA–HCl). Anthranilic acid (2.19 g, 16 mmol) was dissolved in 350 mL of H_2O and about 1 M HCl to maintain a pH around 0.2–0.5. A 50-mL aqueous solution of $Na_2S_2O_8$ (3.81 g, 16 mmol) was added in slowly. The procedure is similar to that for PAN except for a longer reaction time of 48 h. The brownish-black powder obtained was soluble in NMP, DMSO, diethylene glycol, and aqueous NaOH to give reddish-brown solutions.

Synthesis of Poly(anthranilic acid) (PANA). PANA was synthesized in the same way as that described for PANA–HCl but without the HCl. A dark brown precipitate was formed after 24 h, and the polymer obtained was filtered and dried after 96 h.

Synthesis of Doped Copolymers (CP21–HCl, CP11–HCl, and CP12–HCl). A 50-mL solution of $Na_2S_2O_8$ (3.8 g, 16 mmol) was added dropwise with constant stirring to a 100-mL solution containing aniline (0.75 g, 8 mmol), anthranilic acid (1.1 g, 8 mmol), and HCl to maintain a pH of about 0.1 to give a copolymer of feed ratio of 1:1. The polymerization was carried out for 48 h. The polymer powder formed was filtered and dried in a desiccator over P_2O_5. The solubility of the greenish-black powder obtained in NMP and DMSO increased with the amount of anthranilic acid present. Thin brittle films can be cast from the NMP solution. The coding for the different copolymers prepared based on different feed ratios of the monomers, their yields, and their conductivities are given in Table I. The general structure of the copolymer is given in Figure 1.

Elemental Analysis. Elemental analysis was performed by the Microanalytical Laboratory in our Department, using the Perkin-Elmer C, H, N analyzer (Model 240-C). The halogen content was determined by the oxygen flask method.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy analysis was carried out using a VG ESCA/

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Table I
Bulk and Surface Stoichiometries of Homo- and Copolymers

sample	yield (%)	stoichiometries (bulk)	stoichiometries (XPS)	conductivities (S cm^{-1})
PAN–HCl	67.0	$C_{6.1}H_{5.4}N_{1.0}Cl_{0.48}S_{0.01}$	$C_{7.9}N_{1.0}Cl_{0.24}O_{0.64}S_{0.01}$	24
CP21–HCl	50.1	$C_{6.7}H_{5.7}N_{1.0}Cl_{0.43}S_{0.13}$	$C_{7.9}N_{1.0}Cl_{0.21}O_{1.1}S_{0.10}$	4
CP11–HCl	39.2	$C_{6.8}H_{5.4}N_{1.0}Cl_{0.41}S_{0.01}$	$C_{8.4}N_{1.0}Cl_{0.17}O_{1.42}S_{0.04}$	7×10^{-3}
CP12–HCl	32.1	$C_{7.5}H_{5.7}N_{1.0}Cl_{0.39}S_{0.01}$	$C_{10.1}N_{1.0}Cl_{0.15}O_{2.0}S_{0.14}$	2×10^{-5}
PANA–HCl	8.1	$C_{9.7}H_{6.0}N_{1.0}Cl_{0.28}S_{0.08}$	$C_{12.4}N_{1.0}Cl_{0.13}O_{3.7}S_{0.01}$	3×10^{-8}
PANA	6.9	$C_{6.9}H_{5.1}N_{1.0}S_{0.12}$		$<1 \times 10^{-10}$

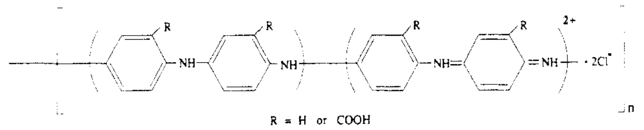

Figure 1. General structure of aniline–anthranilic acid copolymers.

SIMSLAB MK II with Mg *Kα* radiation. The vacuum-dried sample was mounted on a standard VG sample holder by double-sided Scotch tape. The binding energies were referenced to the hydrocarbon component in the C1s envelope, defined to be 285.0 eV to compensate for surface charging. The surface stoichiometries were obtained from peak area ratios corrected for their appropriate sensitivity factors. An error of ±15% in surface stoichiometries can be expected.

Thermal Analysis. The samples in powder form (10–20 mg) were examined with the Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer and a DSC 2910 module. A heating rate of 10 °C min^{-1} was selected for both the TG and DSC under a dynamic dry air flow of 75 cm^3 min^{-1}. The thermal studies were made in the temperature range of room temperature to 750 °C and 350 °C for TG and DSC, respectively.

Electrical Conductivity. Conductivity measurements were made on a four-point probe connected to a Keithley voltmeter constant-current source system. The samples were in the form of compacted disk pellets 12.7 mm in diameter and ≈1 mm thick. Six measurements were made on each of duplicate samples.

Ultraviolet–Visible Spectroscopy. The UV–vis spectra of very dilute solutions of the polymer bases in NMP were recorded on a Shimadzu UV-160 UV–visible spectrometer at room temperature.

IR Spectroscopy. The infrared spectra of the polymers in KBr disks form were recorded on a Shimadzu IR-470 infrared spectrometer at room temperature.

Results and Discussion

The general structure of the homopolymers and copolymers is shown in Figure 1. It can be seen from Table I that the yield decreases with an increase in the proportion of anthranilic acid in the comonomer feed. This is consistent with the proposed mechanism for the polymerization of aniline which involves electrophilic substitution of the comonomer by the growing polymer chains. The electron-withdrawing carboxylate group decreases the reactivity of anthranilic acid, and together with its steric effect, retards the participation of anthranilic acid in the polymerization.

In Table I, a comparison is given for the bulk and surface stoichiometries together with the conductivities of the homopolymers and the copolymers. Both the surface and the bulk results show a gradual decrease in the amount of chloride incorporated as the amount of PANA increases in the comonomer feed, dropping to about 55% of the amount found in PAN–HCl. The higher-than-theoretical carbon and oxygen values measured by XPS, especially in the case of PAN–HCl, can be attributed to oxidation during and after polymerization, water bound to the polymer salt, and hydrocarbon contamination usually found in XPS experiments.

On close examination, the results in Table I suggest that a correlation exists between the conductivity and the amount of the anthranilic acid and chloride present in the system. In order to understand this better, the electronic structure and protonation level of the homopolymer and copolymers as well as the chemical state of the dopant have been carefully studied by XPS. The C1s, N1s, and Cl2p core level spectra for PAN–HCl, CP11–HCl, and PANA–HCl are shown in Figures 2–4, respectively, and the numerical for these and other copolymer systems CP12–HCl and CP21–HCl are summarized in Table II. For PAN–HCl, the C1s can be deconvoluted into four components, each with a fwhm (full width at half-maximum) of 1.6 eV; *C*—C or *C*—H (284.8 eV), *C*—N, *C*—Cl, or *C*=N (286.0 eV), *C*=N$^+$ or C—N$^+$ (287.1 eV), and *C*=O (288.3 eV). The C=O functionality can be attributed partly to the formation of aromatic carbonyl species during polymerization or by aerial oxidation. For CP11–HCl and PANA–HCl, the extra component at the

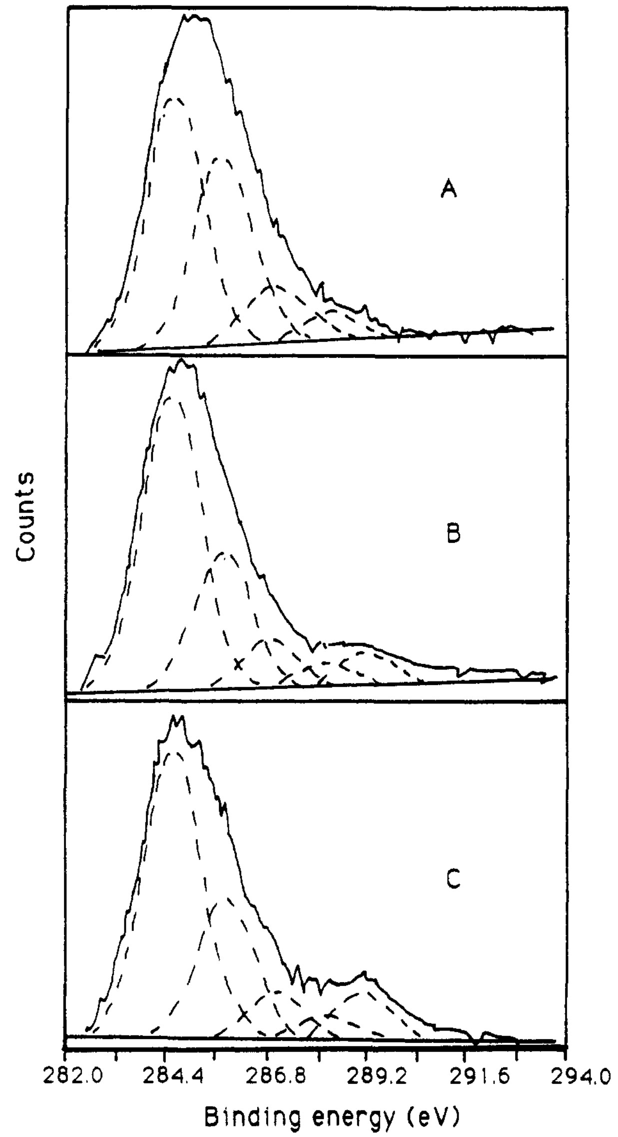

Figure 2. XPS C1s spectra of PAN–HCl (A), CP11–HCl (B), and PANA–HCl (C).

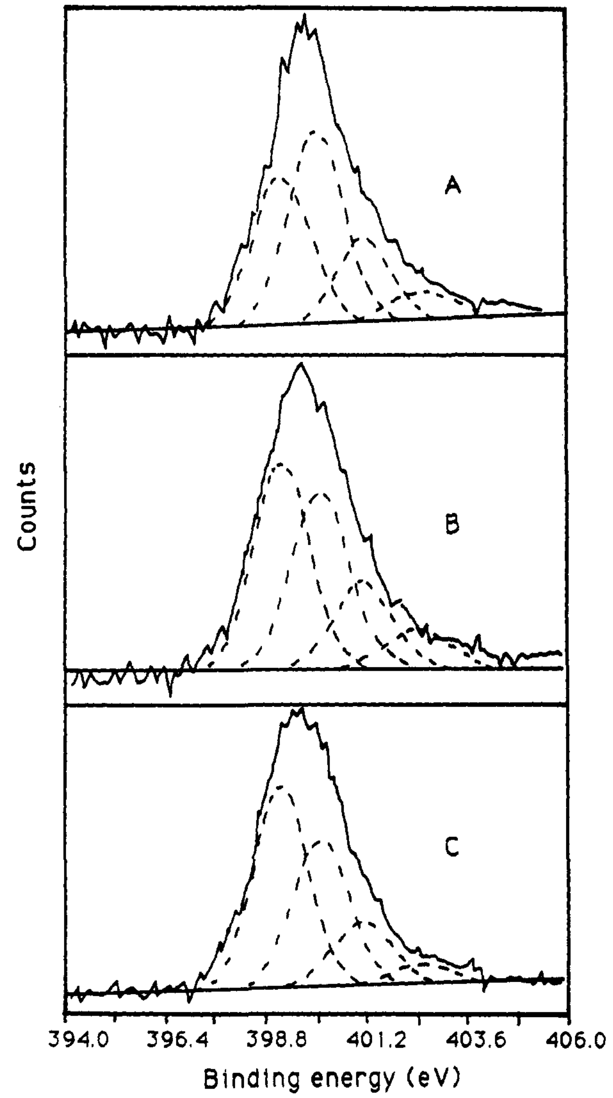

Figure 3. XPS N1s spectra of PAN-HCl (A), CP11-HCl (B), and PANA-HCl (C).

high binding energy of about 289.2 eV indicates the existence of the carboxylate group, O—C═O, the area ratio of which provides a direct measure of the amount of anthranilic acid in the copolymer, as shown in Table III. This is important as other techniques such as IR and NMR used in this work have failed to provide a measure of the composition of the copolymers. The four component peaks for the N1s core level for all the polymers (see Figure 3), each with fwhm = 1.5 eV, can be interpreted as follows: C═*N* (399.4 eV), C—*N* (400.2 eV), C═N^+ (401.2 eV), and C—N^+ (402.5 eV) based on the increasing positive charge on the nitrogen atom which leads to a higher binding energy of the core electrons. The doping level, as measured by the percent area of the positively charged N1s components at 401.2 and 402.5 eV, falls within a narrow range of 20–30%. The Cl2p envelope can be deconvoluted into six components, each with fwhm of 1.6 eV, corresponding to three different chemical environments split into doublets ($Cl2p_{1/2}$ and $Cl2p_{3/2}$) and separated by 1.5 eV with the area ratio of 2:1. The three chlorine environments are C═N^+Cl^- (197.6 eV), C—N^+Cl^- (199.1 eV), and H—*Cl* and C—*Cl* (200.6 eV). All the O1s envelopes of the doped copolymers and PANA-HCl have three components which have been assigned as C═*O* (531.0 eV), C—*O* (532.5 eV), and H_2O (533.4 eV). Interestingly, in all cases, the amount of C═O component is greater than the C—O component (see Figure 5 for example). This deviation from the theoretical 1:1 C═O to C—O ratio may be due to the presence of a small amount of quinoid imine formed by oxidative degradation, hydrolysis, and aerial oxidation, as suggested by Monkman.[25] The amount of oxygen in PAN-HCl is very small and no deconvolution was attempted. It is worth noting that all samples contained water.

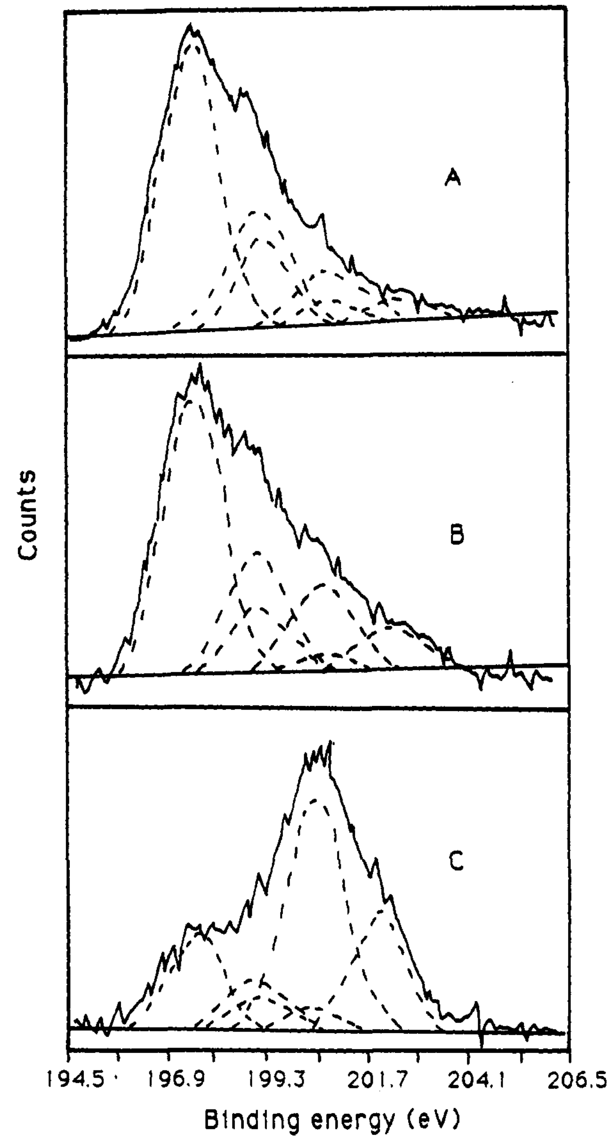

Figure 4. XPS Cl2p spectra of PAN-HCl (A), CP11-HCl (B), and PANA-HCl (C).

The chemical shifts of the different environments for the C1s, N1s, and Cl2p core levels are in good agreement with those previously reported.[23-26] In the present work the Cl^-:N^+ ratio for PAN-HCl is close to unity (1.01), as found previously.[27] For the copolymers, however, the Cl^-:N^+ ratio shown in Table III decreases steadily with an increasing proportion of anthranilic acid in the comonomer feed. This means that some of the nitrogen atoms have been self-doped by the protons of the carboxylate groups in the copolymer in order to maintain charge neutrality. A similar self-doped mechanism has been proposed by Epstein[26] on the basis of XPS studies. The results obtained in the present work indicate that although the percent of protonation lies between about 20 and 30%, the conductivity depends markedly on the type of proton involved. Self-doping by the carboxylic acid group seems very much less effective than the corresponding doping by HCl. This can be rationalized on the basis of the effects of the carboxylate substituent on the polymer structure. First, the strong intramolecular interaction between the COO^- groups and the polaronic nitrogen atoms or H bonding

Table II
XPS Binding Energies and Area Ratios for Cls, Nls, and Cl2p Core Levels

		area ratios				
	binding energy (eV)	PAN-HCl	CP21-HCl	CP11-HCl	CP21-HCl	PANA-HCl
Cls	284.6	47.5	49.9	56.0	51.5	51.6
	285.5	36.3	29.7	24.5	29.0	25.4
	287.1	11.4	11.3	8.1	7.3	9.1
	288.3	4.8	3.1	4.2	3.7	4.1
	289.2		6.0	7.3	8.5	9.7
Nls	399.2	34.6	36.6	41.8	41.0	45.5
	400.2	45.1	33.9	34.2	37.8	34.1
	401.2	15.1	20.3	16.6	16.5	15.4
	402.4	5.2	9.2	7.4	4.6	5.1
Cl2p	197.5	50.4	40.2	45.0	36.0	17.2
	199.0	21.8	16.6	19.3	14.2	8.6
	199.1	13.1	21.2	11.1	7.4	5.9
	200.6	2.9	7.3	2.3	1.4	3.2
	200.6	9.7	10.2	14.5	28.2	43.2
	202.1	2.1	4.6	7.7	12.8	21.9

Table III
Summary of XPS Results

sample	% COOH	% Cl$^-$	% N$^+$	Cl$^-$:N$^+$	conductivities (S cm^{-1})
PAN-HCl	0.00	88.2	22.3	1.01	24.0
CP21-HCl	6.04	85.3	29.5	0.61	4.0
CP11-HCl	7.30	77.7	24.0	0.55	7.0×10^{-3}
CP12-HCl	8.50	59.0	21.1	0.42	2.0×10^{-5}
PANA-HCl	9.70	34.9	20.5	0.22	3.0×10^{-8}

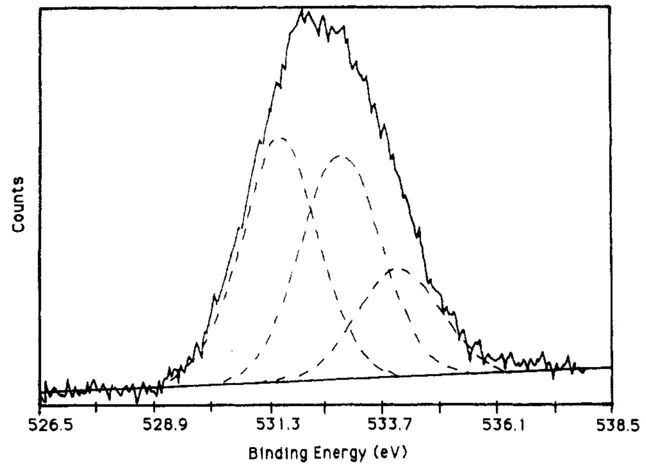

Figure 5. XPS Ols spectrum of CP11-HCl.

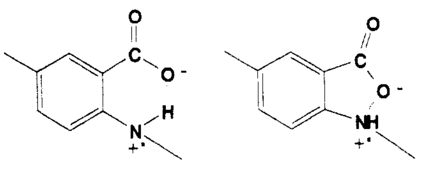

Figure 6. Intramolecular interaction between the carboxylic group and polaronic nitrogen atom.

can give rise to favorable five- or six-membered chelates, as shown in Figure 6. The movement of electrons is more localized in these structures. As a result, the conductivity is adversely affected, as reported by Epstein.[28] Second, the steric effect of the carboxylate group is likely to disrupt the overlapping of orbitals, hence lowering the degree of conjugation, by forcing the aromatic rings out of plane relative to each other. This will be discussed later based on the UV-vis spectroscopic results. Third, a further decrease in the extent of conjugation can be envisaged when intermolecular interaction between the $-COO^-$ group and hydrogen on the adjacent phenyl takes place in the present system (see Figure 7). All these factors contribute to the lowering of conductivity.

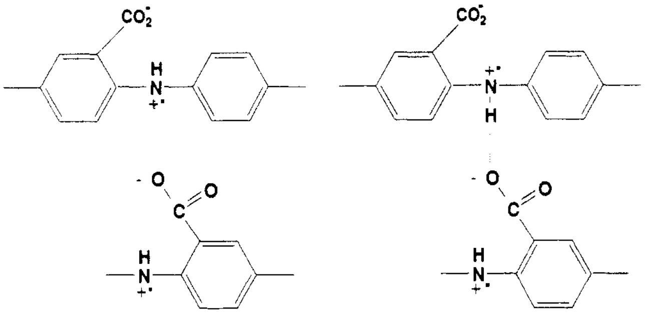

Figure 7. Intermolecular interaction between the carboxylic acid group and polaronic nitrogen atom.

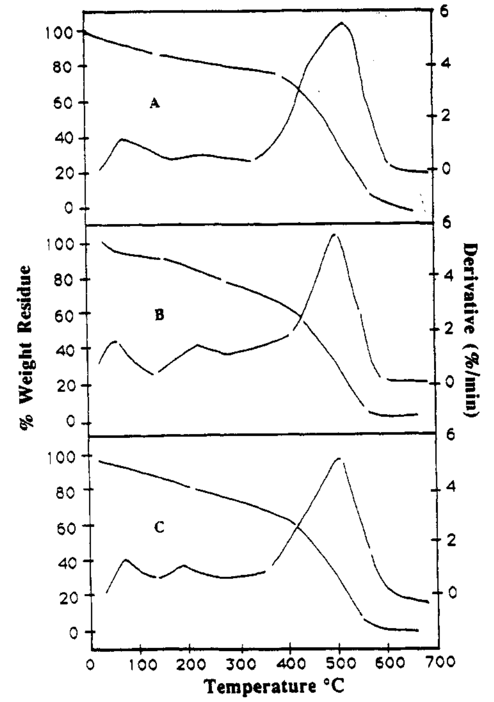

Figure 8. TG thermograms of PAN-HCl (A), CP11-HCl (B), and PANA-HCl (C).

The TG and DSC curves for PAN-HCl, PANA-HCl, and CP11-HCl are given in Figures 8 and 9, respectively. The weight loss patterns are in good agreement with previous reports on polyaniline.[29-31] The first weight loss at around 40–100 °C can be attributed to the volatilization of solvent or surface HCl. The second small step at between 150 and 260 °C is due to the loss of dopant HCl and, in the case of CP11-HCl and PANA-HCl, the concurrent evolution of CO$_2$ (12–15% compared to 8% in

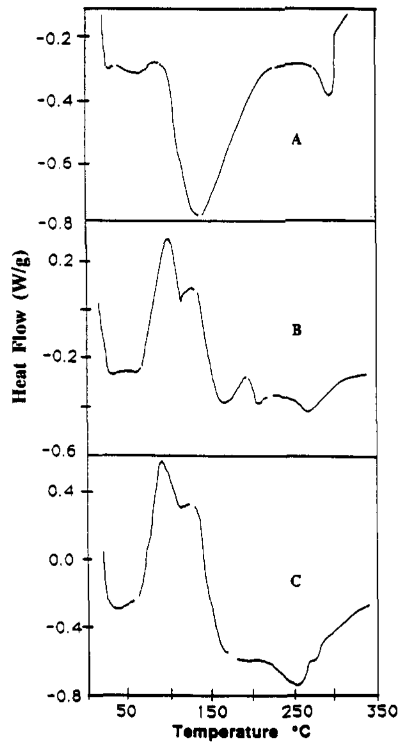

Figure 9. DSC thermograms of PAN-HCl (A), CP11-HCl (B), and PANA-HCl (C).

PAN). The overall decomposition patterns between 400 and 600 °C for the three polymers are almost identical with the maximum rate of weight loss of about 5% min^{-1} at 530 °C. The use of the copolymer offers no advantage in terms of heat stability over PAN.

The large DSC endothermic peak in Figure 9a for PAN-HCl between 120 and 210 °C correlates with the loss of the HCl dopant in the TG study, and the enthalpy for this process is 193.3 J/g. The glass transition (T_g) temperature reported for the PAN film at about 140 °C[32] was not observed as it may have been masked by the overlapping transition in the polymer. Moreover, a different form (powder) was used in this work. For the copolymer CP11-HCl and homopolymer PANA-HCl, the two exothermic peaks at 95 and 136 °C may be related to the intramolecular and intermolecular hydrogen bonding (H bonding) made possible by the structure of the polymer, as shown in Figures 6 and 7. The degree of H bonding is particularly high in the doped form, as the hydrogens attached to the protonated amine or imine nitrogen atoms are made more electropositive. Maximum H bonding occurs, especially in the case of intermolecular interaction, when the polymer chains have acquired enough energy to orientate and align themselves above the T_g at which segmental rotation through the C–C single bond is possible. The endothermic drift between 250 and 300 °C can be attributed to morphological changes within the polymer matrix. Examination under the microscope of temperatures up to 300 °C did not show any flow behavior.

Usually, the association between molecules or polymer chains through the formation of hydrogen bonds is responsible for higher thermal stability, as more energy is required to overcome the hydrogen bonds formed prior to the decomposition of the polymer backbone. This, however, is not observed in the present study, as indicated by the very similar TG curves obtained for the homopolymers and copolymer. This implies that in the undoped state after the expulsion of the HCl dopant, the interaction between the chains due to hydrogen bonding is diminished to the extent that it has no influence on the subsequent thermal behavior of the polymer.

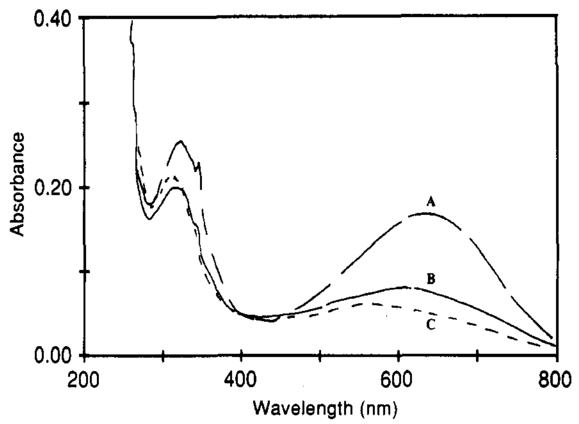

Figure 10. UV-vis spectra for CP21 (A), CP11 (B), and CP12 (C).

The UV-vis solution spectra of copolymers CP21, CP11, and CP12 are compared in Figure 10. The spectra all consist of two major absorption bands. The first one at 312–321 nm (3.97–3.86 eV) is assigned to the π–π^* transition on the basis of earlier studies on polyaniline[33] and is related to the extent of conjugation between adjacent phenyl rings in the polymer chain. It exhibits a hypsochromic shift from 321 to 312 nm as the proportion of the anthranilic acid increases in the copolymer. The second absorption band is assigned to the "exiton" transition caused by interchain or intrachain charge transfer.[34] This band has been found to be dependent on the overall oxidation state of the polymer.[35,36] It also shows a hypsochromic shift from 639 nm (1.94 eV) in CP21 to 571 nm (2.17 eV) in CP12. The extended conjugation of π orbitals, believed to be responsible for conductivity in polymers, requires coplanarity of the atoms involved in the π-cloud delocalization for maximum resonance interaction. The hypsochromic shifts suggest that the steric effect of the carboxylate groups in the polymer chain cause perturbation of the coplanarity of the π system, hence lowering the degree of conjugation as well as hindering charge transfer between chains. The band gap is increased which would lead to the observed decrease in conductivity, in accordance with that reported for sulfonic ring-substituted polyaniline.[33-35]

With the exception of the C═O absorption band at about 1680 cm^{-1}, the IR spectra of the copolymers show the same characteristic absorption as that of PAN. This indicates a low content of anthranilic acid units in the composition of the copolymers. The relative intensity of the C═O stretching band increases as expected with increases in the loading of anthranilic acid. Attempts to determine the copolymer composition from the intensity of this band were unsuccessful due to its poor resolution.

Conclusions

The soluble PANA homopolymers (with or without external dopant HCl) exhibit very low conductivities compared to PAN. For the copolymers, the solubility increases while the conductivity decreases with the amount of anthranilic acid in the comonomer feed. XPS results indicate a self-doping mechanism by the carboxylate group. Whilst the degree of protonation for all systems varies between 20 and 30%, as determined by the area ratio of the charged to total nitrogen environment, it is important to note that the conductivity depends on the type of doping in operation. Self-doping by the carboxylate group is much less effective than external doping by HCl. This can be explained in terms of localization of polarons through the interaction between the carboxylic groups and the polaronic nitrogens in the polymer chain. The degree of conjugation is also lowered due to the increase in the torsional angles between the aromatic rings in order to relieve steric strain exerted by the bulky –COOH group. This is supported by the UV–vis spectra of polymers which indicated a hypsochromic shift of the π–π^* transition band with an increasing proportion of anthranilic acid.

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Registry No. PAN–HCl, 89183-45-9; PANA–HCl, 143077-62-7; PANA, 118337-98-7; (AN)(ANA)·xHCl (copolymer), 143077-63-8.