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Wadia Dhaoui^a; Souhaira Hbaieb^a; Hedi Zarrouk^a; Abdellatif Belhaj Mohamed^b

^a Research Unit of Physical Chemistry of Solid Materials, Faculty of Sciences, University of Tunis, Tunis, Tunisia ^b Laboratory of Photovoltaics and Semiconductors, National Institute of Scientific and Technical Research, Tunis, Tunisia

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Investigation of Spectral Properties, Thermal Stability, and Morphology in Polyaniline Doped with Chlorocarboxylic Acids

Wadia Dhaoui, Souhaira Hbaieb, and Hedi Zarrouk

Research Unit of Physical Chemistry of Solid Materials, Faculty of Sciences,
University of Tunis, Tunis, Tunisia

Abdellatif Belhaj Mohamed

Laboratory of Photovoltaics and Semiconductors, National Institute of Scientific
and Technical Research, Tunis, Tunisia

Abstract: The morphology of polyaniline (PANI), granular or tubular, depends on the acidity conditions during the reaction rather than on the chemical nature of the acid. In reference to acetic acid in which media nanotubes had been observed, dichloroacetic acid (DCA) and trichloroacetic acid (TCA) were used to synthesize polyaniline by the oxidative polymerization technique. Characterization by Fourier-transform infrared (FTIR), UV-visible, and electron paramagnetic (EPR) spectroscopy techniques indicated that the polymers are in the protonated emeraldine form and suggest that the protonation of PANI in media containing such acids was achieved with the help of sulfuric acid produced during the reaction from ammonium peroxydisulfate. The conductivity of polyaniline prepared in DCA was 0.04 S cm^{-1} and 0.5 S cm^{-1} in TCA. The thermal stability of polyaniline salts was tested by thermogravimetric analysis and a three-step decomposition pattern was observed. Wide-angle X-ray diffraction (WAXD) study showed enhanced crystallinity in polyaniline prepared in TCA. The morphology is

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Address correspondence to Wadia Dhaoui, Research Unit of Physical Chemistry of Solid Materials, Faculty of Sciences, University of Tunis, Manar II-2092 Tunis, Tunisia. E-mail: wadia.ammar@planet.tn

discussed in relation to the formation of polyaniline nanotubes reported in the literature.

Keywords: Conducting polymer; Dichloroacetic acid; Morphology; Polyaniline; Trichloroacetic acid

INTRODUCTION

Polyaniline (PANI) has emerged as one of the most promising conducting polymers, which exhibits excellent environmental stability in its conducting form^[1,2] and ease of synthesizing and doping with various acids.^[3] It is typically prepared by the oxidation of aniline with ammonium peroxydisulfate in aqueous acidic medium (Figure 1). Utilizing acids with different chemical structures results in modifications of PANI properties, such as conductivity,^[4] surface morphology,^[5] solubility,^[6] and mechanical properties.^[7] Several examples highlight the need to produce conducting polymers with a variety of counterions.^[8–11] In most oxidative polymerizations, solutions of hydrochloric acid have been used a reaction medium.

Common inorganic acids and organic sulfonic acids are strong enough to produce favorable conditions for the polymerization of aniline. In contrast, most carboxylic acids do not provide sufficient acidity for efficient polymerization of polyaniline, and, consequently, the conductivity of PANI prepared in their presence is reduced. Considerable efforts have been made towards the synthesis of PANI containing carboxylic acids.^[12–18] For particular applications, such as antistatic coatings, the conductivities need not be high, and finding a procedure by which PANI can be easily processed from aqueous solutions or colloidal dispersions has remained an interesting goal.

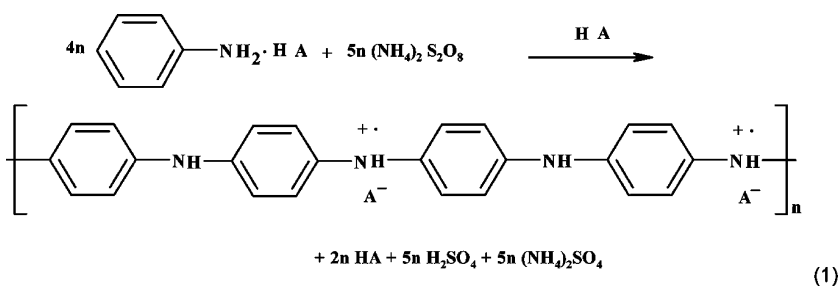


Figure 1. Oxidation of aniline salts with various acids (HA) with ammonium peroxydisulfate yields protonated polyaniline. Sulfuric acid and ammonium sulfate are produced at the same time.

The preparation of polyaniline nanotubes^[19,20] and nanowires^[21,22] has recently emerged as a new research field. PANI prepared in strong acids has a good conductivity and granular morphology, PANI obtained in weak acids has lower conductivity but interesting nanotubular morphology. The formation of PANI nanotubes by polymerizing aniline in water and in solutions of acetic acid has recently been demonstrated.^[23] In the present article, we report the preparation of PANI in the presence of dichloroacetic (DCA) and trichloroacetic (TCA) acids. Such a system has already been reported in the literature.^[24–26] The properties of products are discussed in relation to polymerization in acetic acid solutions.

EXPERIMENTAL SECTION

Preparation of Polyaniline

Aniline (p.a., Merck) was distilled under reduced pressure prior to use. All other chemicals were analytical grade reagents and used as received. Distilled water was used in the experiments. Chemical oxidation of 0.2 M aniline was carried out in an aqueous acidic media containing 1.2 M of dichloroacetic or trichloroacetic acid. The polymerization was started by the drop-wise addition of an aqueous solution of 0.25 M ammonium peroxydisulfate to the acidified solution containing aniline at 0°–5°C under constant stirring. Then, the oxidizing agent was added and the reaction mixture was left for 24 h. The precipitated polyaniline salt was separated by filtration, rinsed with a corresponding solution of acid, and dried at ambient temperature in vacuum.

Characterization of Polyaniline

Elemental analysis was made by using Elementar Vario El analyzer. Energy dispersive spectroscopy (EDX) analysis and scanning electron microscopy (SEM) images were obtained on a Philips XL 30 apparatus, at an accelerating voltage of 20 kV. UV-visible spectra of polymer solutions in *m*-cresol were recorded by using a Perkin-Elmer Lambda 2 UV-Vis spectrophotometer. Infrared measurements in the range 400–4000 cm⁻¹ were made with a fully computerized Bruker IFS 55 Equinox FTIR (Fourier transform infrared) spectrometer (64 scans per spectrum at 4 cm⁻¹ resolution). The spectra were corrected for the presence of moisture and carbon dioxide in the optical path. The samples were prepared in pellet form using spectroscopic-grade potassium bromide. Electron paramagnetic (EPR) spectra of the sample were obtained on a Varian E109 spectrometer operating in the X band. DC conductivity of samples was measured at room temperature by a four-point van der

Pauw method on pellets compressed in a hydraulic pressing at 1 GPa. The polymers were subjected to thermal degradation studies on a thermal analyzer system, Setaram TGDTA 92, fitted with a data station. The analysis was carried out at 40° to 900°C at a heating rate of 10°C min⁻¹ under nitrogen atmosphere. Wide-angle X-ray diffraction spectra of PANI powders were obtained using a Philips PW 3040 X-ray diffractometer using Cu-K_α radiation of wavelength 0.154 nm at continuous scan speed of 0.02 deg min⁻¹.

RESULTS AND DISCUSSION

The precipitation polymerization of aniline for the single-step preparation of conducting PANI starts in a homogeneous medium, and, consequently, water-soluble organic acid should be used. Moreover, the neutralization reaction of aniline with these acids should produce water-soluble salts. These conditions are met by many carboxylic acids.^[27,28] Two acids newly tested in this study are dichloroacetic and trichloroacetic acids. In both cases, the addition of ammonium peroxydisulfate, used as an oxidant agent, started the polymerization of aniline salt. The relative yield of PANI, expressed as PANI-to-aniline weight ratio, was 48.9% for polymerization in DCA and 63.8% in TCA. Depending on the chemical structure of the acid, some differences in the final PANI products were observed.

Elemental Composition

The chemical composition of polyaniline salts was determined by elemental analysis (Table I). Oxidative chemical polymerization of aniline in

Table I. Theoretical and experimental elemental composition of polyaniline prepared in solutions of dichloroacetic or trichloroacetic acid

Sample	C (%)	H (%)	N (%)	Cl (%)
PANI-TCA				
Experimental	58.17	4.51	9.67	16.22
Calculated for PANI-(TCA) _{0.22} · 0.5H ₂ O	57.04	4.22	10.33	17.29
PANI-DCA				
Experimental	62.34	4.95	10.64	10.25
Calculated for PANI-(DCA) _{0.19} · 0.5H ₂ O	61.73	4.74	11.28	10.87

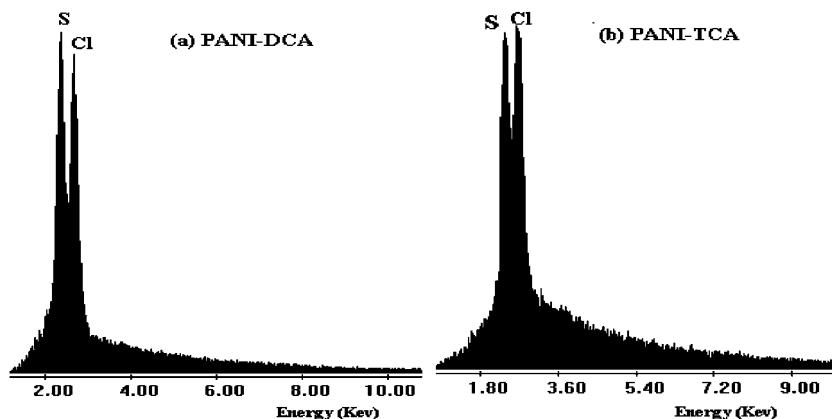


Figure 2. EDX spectra of polyaniline prepared in the presence of (a) dichloroacetic acid or (b) trichloroacetic acid.

aqueous acid medium yields PANI in emeraldine form (Figure 1). It has been found that the doping ratio depends on the acid, and for PANI prepared in DCA it is 0.19 of acid molecules per 2 aniline constitutional units, whereas in TCA this number is slightly higher, 0.22. The relatively low molar ratio of the acid to PANI suggests that other acid molecules participate in the protonation of PANI chains. Sulfuric acid, produced during the oxidation of PANI as a by-product (Figure 1), is obviously able to provide the competitive protonation. It has been reported that the complete protonation of PANI is obtained if the oxidation is carried out in water^[29] or in solutions of weak acids,^[30] like acetic acid.^[23] Both DCA and TCA are stronger than acetic acid and are thus able to be at least partly associated with PANI backbone.

The EDX spectra of PANI indeed reveal that both the chlorine and sulfur peaks are present in the polymers, confirming the presence of both chloroacetic and sulfuric acids groups in PANI salts (Figure 2).

Electronic Absorption Spectra

The samples are partly soluble in *m*-cresol. Their solubility is thus somewhat improved with respect to common PANI protonated with inorganic acids but it is still far from being of importance for practical processing. The UV-visible spectra of the soluble parts in *m*-cresol of PANI salts are shown in Figure 3. Three peaks at 320, 420, and 800 nm together with a weak band at 600 nm are discernible in the spectra. The peak at 320 nm corresponds to π - π^* transition of the benzenoid rings,^[31] while the peaks

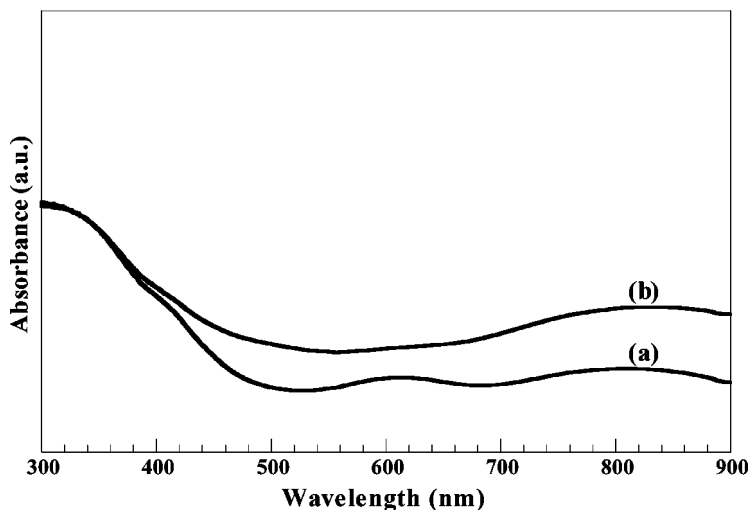


Figure 3. UV-visible spectra of polyaniline doped with (a) dichloroacetic acid or (b) trichloroacetic acid recorded using *m*-cresol as the solvent.

at 420 nm and 800 nm can be assigned to the localized polarons that are characteristic of the protonated PANI.^[32] The UV-vis spectra prove that PANI prepared in chloroacetic acids TCA and DCA is protonated.

FTIR Spectra

FTIR spectra of both synthesized samples display the features typical of protonated PANI (Figure 4). The main absorption bands having usual significance are summarized in Table II. They highlight all characteristic peaks observed in PANI sulfate,^[33] and the strong absorption band carbonyl group, characteristic of carboxylic anions, is absent in the spectra. This confirms the low proportion of chloroacetic acids in PANI. The absorption band at 1570 cm^{-1} suggests that the PANIs have quinone structure. The lower frequency mode at 1490 cm^{-1} depicts the presence of benzenoid rings. The presence of these two bands clearly shows that these polymers are constituted of amine and imine nitrogen-containing units, i.e., that they have a standard structure.

Electron Paramagnetic Resonance Spectra

The EPR spectra of polyaniline salts prepared in DCA and TCA solutions exhibit a single signal without hyperfine structure (Figure 5). The

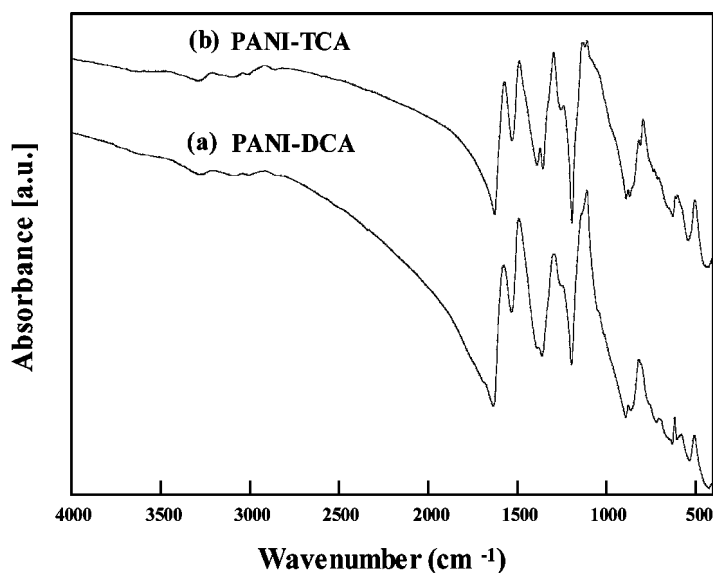


Figure 4. FTIR spectra of polyaniline doped with (a) dichloroacetic acid or (b) trichloroacetic acid.

shape of the EPR signal is the same for the two polymers. The g values are 2.0054 and 2.0046 for the samples prepared in DCA and TCA solutions, respectively, the line width being 1.44 and 1.47 G. Delocalized free

Table II. Assignments of the main peaks in the FTIR spectra of polyaniline salts^[34]

PANI-TCA	PANI-DCA	Peak assignments ^a (wavenumbers in cm^{-1})
500	500	Bend. of C–C on Q
620	600	Bend. of C–C on B
700	700	Bend. of C–C on B, Q
820	820	Bend. of C–H (out-of-pl.) on B (p-disubst.)
1141	1150	Bend. of C–H (in-pl.), mode of N=Q=N, Q=N ⁺ H–B, B–N ⁺ H–B
1238	1240	Str. of C–N ⁺
1297	1300	Str. of C _{ar} –N
1487	1486	Str. of N–B–N ring
1576	1572	Str. of N=Q=N ring

^aB = benzene ring, Q = quinoid ring, Str. = stretching, Bend. = bending.

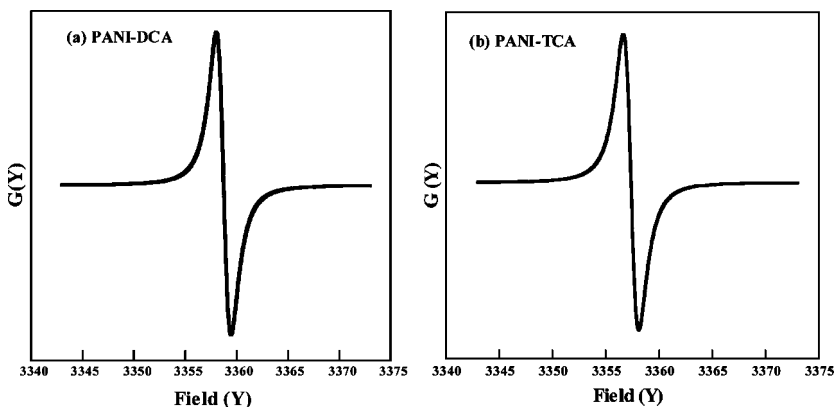


Figure 5. EPR spectra of polyaniline prepared in (a) DCA or (b) TCA solutions.

radicals thus exist in the PANI backbone. The A/B ratio of the area of the positive to the negative peak remains constant for the two polymers and is close to unity, 1.00 and 1.02, thereby indicating that the spins are of the free-electron type.

Conductivity

The DC conductivity of the PANI prepared in the solutions of DCA and TCA were 0.04 S cm^{-1} and 0.5 S cm^{-1} . These values are comparable to the conductivity of PANI prepared in the absence of any acid,^[23] 0.083 S cm^{-1} . PANI prepared similarly in the solution of acetic acid was reported to have a conductivity^[23] of 0.27 S cm^{-1} . The fact that chloroacetic acids are stronger than acetic acid is thus not positively reflected in the conductivity of the products. We can speculate that the oxidation of chloroacetic acids could result in chlorine formation followed by the chlorination of PANI backbone. The polyanilines prepared in the presence of inorganic acids have a typical conductivity of several units of^[29] S cm^{-1} .

Thermogravimetric Analysis

The polyaniline prepared with dichloroacetic and trichloroacetic acids as protonation media exhibits a three-step thermogravimetric decomposition (Figure 6). The first stage is characterized by the loss of water $10 \text{ wt.}\%$ below 130°C . In the second stage between 130° and 420°C , the additional mass loss of $19 \text{ wt.}\%$ was observed and connected with

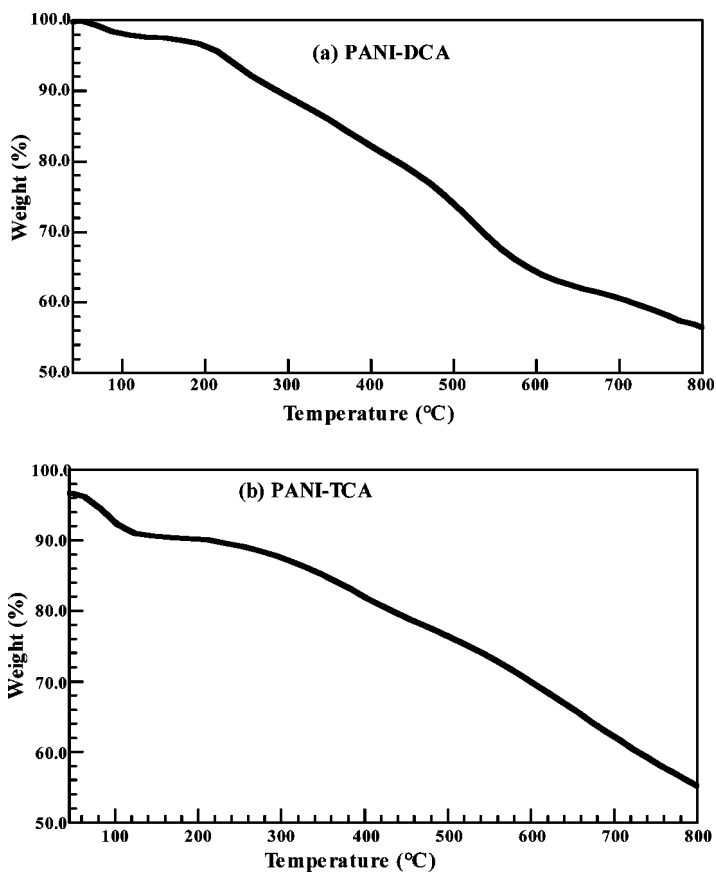


Figure 6. Thermograms of polyaniline doped with (a) dichloroacetic acid or (b) trichloroacetic acid.

the deprotonation of PANI. Degradation of the polymer backbone, accompanied by 45 wt.% mass loss, takes place in the temperature range 420°–760°C. As the experiments have been carried out in nitrogen atmosphere and oxidation has been avoided, the mechanism of decomposition is assumed to be thermal degradation.

Morphology

The morphological aspects of PANI prepared in various acids are quite different (Figure 7). The SEM pictures revealed a granular structure for PANI prepared in TCA (Figure 7(a), (b)). The particles are sharp-edged

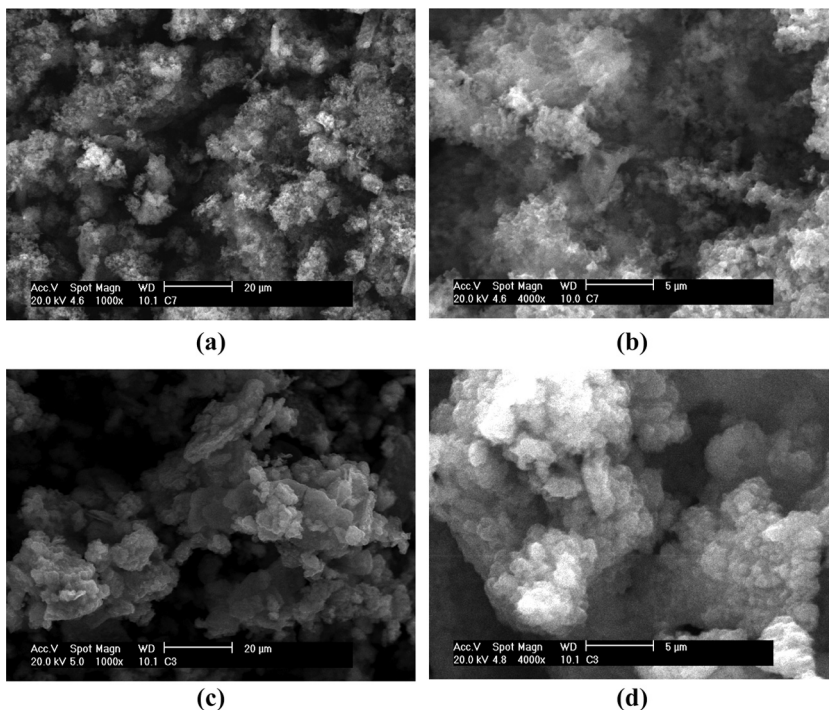


Figure 7. Scanning electron micrographs of PANI prepared in DCA (a) at magnification 1000 \times ; (b) magnification 4000 \times , and in TCA (c) at magnification 1000 \times ; (d) magnification 4000 \times .

with a lamellar structure. In contrast, PANI prepared in DCA exhibits a sponge-like structure derived from the aggregation of small granules (Figure 7(c), (d)). These features remain unchanged even at higher magnifications. The granular structure is typical of PANI that has been prepared in stronger acids, while nanotubular morphology has been reported for polymerization in weak acids, like acetic acid.^[23] These results obtained in the present work clearly suggest that the differences in the morphological patterning are mainly due to the differences in the pH profile during polymerization, which, in turn, depends on the dissociation ability of the respective acids.^[12]

X-ray Diffraction Analysis

The XRD of doped polymers in powder form reveals that the crystallinity of the doped polymers is improved in the samples prepared in TCA

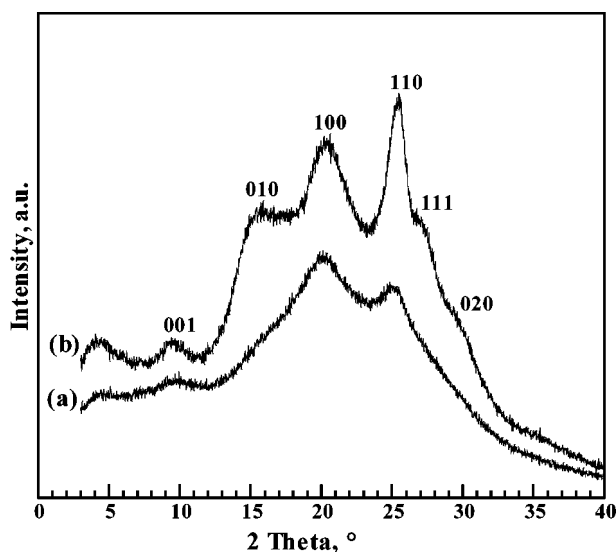


Figure 8. X-ray diffraction patterns of PANI prepared in (a) DCA and (b) TCA.

compared with DCA (Figure 8). The former sample exhibits three main reflections, at $2\theta = 14.7^\circ$, 20.4° , 25.5° , and 27.3° and small reflections at $2\theta = 4.7^\circ$, 9.2° , and 29.9° . These positions are in accordance with an earlier report on the crystallinity of PANI.^[34] The X-ray diffraction pattern of PANI prepared in TCA is compatible with pseudo-orthorhombic lattice symmetry. The indexing for the reflections of largest d spacing is given in Table III. A least-square fit of their 2θ angular position leads to the following pseudo-orthorhombic parameters: $a = 4.26 \text{ \AA}$, $b = 5.89 \text{ \AA}$, $c = 9.29 \text{ \AA}$, and cell volume $v = 233.33 \text{ \AA}^3$. The reflections

Table III. Bragg's angle (2θ), d spacing, intensity, and (hkl) pseudo-orthorhombic indexation of PANI-TCA salt

2θ ($^\circ$)	d (\AA)	Intensity ^a	(hkl)
9.24	9.56	w	001
14.79	5.98	m	010
20.42	4.34	s	100
25.59	3.48	s	110
27.33	3.26	m	111
29.99	2.97	w	020
31.98	2.79	w	112

^as, strong; m, medium; w, weak.

at higher angles above the background amorphous scattering are a good indication that the dopant counter-anion undergoes secondary interaction, inducing higher degree of crystallinity^[35,36]. In contrast, PANI prepared in dichloroacetic acid exhibits an appreciable loss in crystallinity (Figure 8). The peaks present at 2θ of 15° , 20° , 25° , 27° , and 30° have disappeared or broadened, implying a decrease in coherence length of the chain.

CONCLUSIONS

Polyaniline has been synthesized by chemical oxidative polymerization in solutions containing dichloroacetic or trichloroacetic acid. The use of the acid in these experiments controls the initial acidity of the reaction medium while the final acidity is determined by sulfuric acid produced as a by-product during the reaction. The early stages of polymerization and its course that predetermine the chain growth and chain structure, and subsequently the morphology and crystallinity, thus do depend on the nature of added acid and its strength. The nanotubular morphology of polyaniline, reported to be a result of polymerization in acetic acid, has not been observed in the present experiments. The way of protonation is controlled at the final stages of reaction. That is why protonation with sulfuric acid dominates over organic acids and the participation of dichloroacetic and trichloroacetic acids in the samples is marginal. Despite the predominant protonation with sulfuric acid, the conductivity of polyaniline is of the order of 10^{-2} – 10^{-1} S cm^{-1} , possibly due to the chain defects introduced during the growth at reduced acidity. The present study thus hopefully contributes to understanding processes occurring during the oxidation of aniline in the presence of various acids.

REFERENCES

- [1] Yue, J., A. J. Epstein, Z. Zhong, P. K. Gallagher, and A. G. MacDiarmid. (1991). Thermal stabilities of polyanilines. *Synth. Met.* **41**, 765–768.
- [2] Angelopoulo, M., A. Ray, A. G. MacDiarmid, and A. J. Epstein. (1987). Polyaniline: Processability from aqueous solutions and effect of water vapor on conductivity. *Synth. Met.* **21**, 21–30.
- [3] Chiang, J. C. and A. G. MacDiarmid. (1986). Polyaniline: Protonic acid doping of the emeraldine form to the metallic regime. *Synth. Met.* **13**, 193–205.
- [4] Focke, W., G. Wieck, and Y. Wie. (1987). Influence of oxidation state, pH, and counterion on the conductivity of polyaniline. *J. Phys. Chem.* **91**, 5813–5818.
- [5] Stejskal, J., I. Sapurina, J. Prokes, and J. Zemek. (1999). In-situ polymerized polyaniline films. *Synth. Met.* **105**, 195–202.

- [6] Heeger, A. J. (1993). Polyaniline with surfactant counterions: Conducting polymer materials which are processible in the conducting form. *Synth. Met.* **57**, 3471–3482.
- [7] Olinga, T. E., J. Fraysse, J. P. Travers, A. Dufresne, and A. Pron. (2000). Highly conducting and solution-processable polyaniline obtained via protonation with a new sulfonic acid containing plasticizing functional groups. *Macromolecules* **33**, 2107–2113.
- [8] Xuehong, L., Y. N. Hsiao, X. Jianwei, and H. Chaobin. (2002). Electrical conductivity of polyaniline-dodecylbenzene sulphonic acid complex: Thermal degradation and its mechanism. *Synth. Met.* **128**, 167–178.
- [9] Kinlen, P. J., J. Liu, Y. Ding, C. R. Graham, and E. E. Remsen. (1998). Emulsion polymerization process for organically soluble and electrically conducting polyaniline. *Macromolecules* **31**, 1735–1744.
- [10] Hopkins, A. R., P. G. Rasmussen, and R. A. Basheer. (1996). Characterization of solution and solid state properties of undoped and doped polyanilines processed from hexafluoro-2-propanol. *Macromolecules* **29**, 7838–7846.
- [11] Swapna Rao, P., S. Subrahmanya, and D. N. Sathyanarayana. (2002). Inverse emulsion polymerization: A new route for the synthesis of conducting polyaniline. *Synth. Met.* **128**, 311–316.
- [12] Patil, R. C., S. F. Patil, I. S. Mulla, and K. Vijayamohan. (2000). Effect of protonation media on chemically and electrochemically synthesized polyaniline. *Polym. Int.* **49**, 189–196.
- [13] Palaniappan, S. (2001). Chemical and electrochemical polymerization of aniline using tartaric acid. *Eur. Polym. J.* **37**, 975–981.
- [14] Laska, J., J. Widlarz, and E. Wozny. (2002). Precipitation polymerization of aniline in the presence of water-soluble organic acids. *J. Polym. Sci. Part A Polym. Chem.* **40**, 3562–3569.
- [15] Stejskal, J., D. Hlavata, P. Holler, M. Trchova, J. Proles, and I. Sapurina. (2004). Polyaniline prepared in the presence of various acids: A conductivity study. *Polym. Int.* **53**, 294–300.
- [16] Dan, A. and P. K. Sengupta. (2004). Synthesis and characterization of polyaniline prepared in formic acid medium. *J. Appl. Polym. Sci.* **91**, 991–999.
- [17] Erdem, E., M. Karakisla, and M. Saçak. (2004). The chemical synthesis of conductive polyaniline doped with dicarboxylic acids. *Eur. Polym. J.* **40**, 785–791.
- [18] Kulkarni, M. V., A. K. Viswanath, R. Marimuthu, and T. Seth. (2004). Synthesis and characterization of polyaniline doped with organic acids. *J. Polym. Sci. Part A Polym. Chem.* **42**, 2043–2049.
- [19] Zhang, Z., Z. Wei, and M. Wan. (2002). Nanostructures of polyaniline doped with inorganic acids. *Macromolecules* **35**, 5937–5942.
- [20] Long, Y., L. Zhang, Y. Ma, Z. Chen, N. Wang, Z. Zhang, and M. Wan. (2003). Electrical conductivity of an individual polyaniline nanotube synthesized by a self-assembly method. *Macromol. Rapid Commun.* **24**, 938–942.
- [21] Huang, J. and R. B. Kaner. (2004). A general chemical route to polyaniline nanofibers. *J. Am. Chem. Soc.* **126**, 851–855.
- [22] Zhang, X., R. C. Y. King, A. Jose, and S. K. Manohar. (2004). Nanofibers of polyaniline synthesized by interfacial polymerization. *Synth. Met.* **145**, 23–29.

- [23] Konyushenko, E. N., J. Stejskal, I. Šeděnková, M. Trchová, I. Sapurina, M. Cieslar, and J. Prokeš. (2006). Polyaniline nanotubes: Conditions of formation. *Polym. Int.* **55**, 31–39.
- [24] Pomfret, S. J., P. N. Adams, N. P. Comfort, and A. P. Monkman. (2000). Electrical and mechanical properties of polyaniline fibers produced by a one-step wet spinning process. *Polymer* **41**, 2265–2269.
- [25] Grzeszczuk, M. and R. Szostak. (2003). Electrochemical and raman studies on the redox switching hysteresis of polyaniline. *Solid State Ionics* **157**, 257–262.
- [26] Venancio, E. C., A. J. Motheo, F. A. Amaral, and N. Bocchi. (2001). Performance of polyaniline electrosynthesized in the presence of trichloroacetic acid as a battery cathode. *J. Power Sources* **94**, 36–39.
- [27] Spinks, G. M., A. J. Dominis, and G. G. Wallace. (2003). Comparison of emeraldine salt, emeraldine base, and epoxy coatings for corrosion protection of steel during immersion in a saline solution. *Corrosion* **59**, 22–31.
- [28] Gok, A. and B. Sari. (2002). Chemical synthesis and characterization of some conducting polyaniline derivatives: Investigation of the effect of protonation medium. *J. Appl. Polym. Sci.* **84**, 1993–2000.
- [29] Stejskal, J. and R. G. Gilbert. (2002). Polyaniline: Preparation of a conducting polymer. *Pure Appl. Chem.* **74**, 857–867.
- [30] Stejskal, J., I. Sapurina, M. Trchova, and J. Prokes. (2002). Protonation of polyaniline with 3-nitro-1, 2, 4-triazol-5-one. *Chem. Mater.* **14**, 3602–3606.
- [31] Inoue, M., R. E. Navarro, and M. B. Inoue. (1989). New soluble polyaniline: Synthesis, electrical properties and solution electronic spectrum. *Synth. Met.* **30**, 199–207.
- [32] Cao, Y., P. Smith, and C. Yang. (1995). Effect of solvent and co-solvents on the processibility of polyaniline: II. Spectroscopic and diffraction studies. *Synth. Met.* **69**, 191–192.
- [33] Trchova, M., J. Stejskal, and J. Prokes. (1999). Infrared spectroscopic study of solid-state protonation and oxidation of polyaniline. *Synth. Met.* **101**, 840–841.
- [34] Pouget, J. P., M. E. Jozefowicz, A. J. Epstein, X. Tang, and A. G. MacDiarmid. (1991). X-ray structure of polyaniline. *Macromolecules* **24**, 779–789.
- [35] Svetlicic, V., A. J. Schmidt, and L. L. Miller. (1998). Conductometric sensors based on the hypersensitive response of plasticized polyaniline films to organic vapors. *Chem. Mater.* **10**, 3305–3307.
- [36] Santos, J. R., J. A. Malmonge, A. J. G. Conceicao-silva, A. J. Motheo, Y. P. Mascareuhas, and L. H. C. Mattoso. (1995). Characteristics of polyaniline electropolymerized in camphor sulfonic acid. *Synth. Met.* **69**, 141–142.