

Synthesis and Characterization of Polyaniline Prepared in Formic Acid Medium

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ABSTRACT: The oxidative polymerization of aniline in formic acid (HCOOH) medium was investigated using formic acid of different strengths (5–25*N*). It was observed that a certain portion of the total polymer (~ 10%) remains soluble in the reaction medium. The UV–visible absorption spectra of the reaction mixtures in dilute and concentrated HCOOH indicate different initial reaction pathways and intermediates occurring under the conditions employed. It was found that the reaction yield and intrinsic viscosity of the polymer were dependent on the synthesis parameters. By contrast, the electrical conductivity was not sensitive to most of these variables. Elemental analysis revealed that the chemical composition of polyaniline (PANI)–formic acid salt is 4 : 2.2, indicating two units of formate anions present per four-unit polymer chain containing 3 : 1 ratio of benzenoid to quinonoid moieties. Spectroscopic results showed that

PANI prepared in HCOOH exists in an emeraldine oxidation state. A transmission electron micrograph of the soluble portion showed a wide distribution of spherical particles of different diameters in the range 20–200 nm. The thermal stability and crystalline structure of PANI–formic acid salt and its base form were ascertained by thermogravimetric analysis and wide-angle X-ray diffraction (WAXD) study, respectively. The base form of the polymer was stable up to 400°C and the acid form showed evolution of formic acid dopant in the temperature range 200–300°C. WAXD study showed a pseudo-orthorhombic crystal structure for PANI–formic acid salt. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 991–999, 2004

Key words: formic acid; infrared spectroscopy; polyaniline; TEM; thermogravimetric analysis (TGA)

INTRODUCTION

One of the attractive features for which polyaniline (PANI) has received wide attention as a conducting polymer is its simplicity of synthesis using chemical¹ and electrochemical² methods. Another interesting feature of the polymerization is the high rate of reaction even at low temperature. Efforts have been made by various researchers to increase the molecular weight of the polymer,^{3,4} to make soluble polyaniline,^{5,6} and to increase the electrical conductivity as well as thermal stability of the polymers.^{5,7} The chemical nature of the reaction intermediates, the exact pathway of chemical synthesis, and the structure of different types of polyaniline have also been the subject of intensive investigation.^{8–11} However, detailed reports on the synthesis of polyaniline in the presence of solvents like formic acid, *N*-methyl pyrrolidone (NMP), and dimethyl sulfoxide (DMSO), for example,

which generally dissolve either low molecular weight polymers or partly high molecular weight polymers, are scanty.

We thus report here the chemical polymerization of aniline in formic acid, in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant. The main objective of the present study was to assess the solubility of the derived polymer, its chemical character, the course of the chemical reaction, and the effect of various reaction parameters on yield, intrinsic viscosity, and electrical conductivity of the polymer.

EXPERIMENTAL

Materials

Aniline (E. Merck, Darmstadt, Germany) was distilled twice under reduced pressure before polymerization. Formic acid (>98 and 85%), aqueous ammonium hydroxide solution (25%), and ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ were analytical reagent grade, obtained from S.D. Fine Chemicals (Mumbai, India), and used as purchased without any further purification.

Synthesis

Aniline was polymerized in formic acid medium at about 2°C using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidizing agent. In

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a typical procedure, 1 mL (0.0107 mol) aniline was dissolved in 25 mL HCOOH (85%). The solution was cooled to about 2°C in an ice bath. A solution of 2.44 g (0.0107 mol) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dissolved in 25 mL HCOOH (85%) was added dropwise into cold HCOOH solution of aniline with constant stirring over a period of 30 min. The mixture was stirred in a magnetic stirrer for another 2 h at about 2°C. The resulting dark green reaction mixture was filtered. The precipitate was thoroughly washed with deionized water and then with methanol. The solid was dried under dynamic vacuum at 50°C. The soluble part of the polymer present in the reaction mixture was separated by filtration. The polymer was then isolated by pouring the solution into excess distilled water and then filtering the precipitate. The green precipitate was thoroughly washed with water and then dried at 50°C under dynamic vacuum. The polymerization of aniline in 85% formic acid using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidant was carried out under different reaction conditions (e.g., variation of reaction temperature, time, and concentration of oxidant). The polymerization behavior of aniline was also studied in formic acid of different strengths (98, 50, and 20%, i.e., 25.0, 13.0, and 5.0N, respectively). The same polymerization procedure was followed in all cases. Basification of the polymers was carried out by stirring 1 g of the acid-doped polymer in 160 mL 3% aqueous NH_4OH solution for 4 h at room temperature. The solid was then filtered, washed with distilled water until free from NH_4OH , and then dried at 50°C under dynamic vacuum.

Characterization

Elemental analysis of both doped and undoped polyaniline was performed on a C, H, N elemental analyzer (Model 2400; Perkin Elmer Cetus Instruments, Norwalk, CT). Intrinsic viscosity $[\eta]$ (dL/g) of polyaniline base was calculated from solution viscosity measurements of 0.1% w/w polymer solutions in concentrated H_2SO_4 (98%) at 35°C using a Ubbelohde capillary viscometer (Cannon-Ubbelohde, State College, PA). The UV-visible spectra was recorded on a UV-visible double-beam double-monochromator spectrometer (Hitachi Model U3200, Ibaraki, Japan) using NMP as the solvent. The FTIR spectra of the polymers were recorded in KBr pellets on an FTIR spectrometer (Model 1600; Perkin-Elmer) with 16 scans at a resolution of 4 cm^{-1} . The polymers were subjected to thermal degradation studies on a thermal analyzer system (Perkin-Elmer 7 series) fitted with a data station. The analysis was carried out from 50 to 650°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Finely divided samples of about 2–3 mg were used. The electrical conductivity of the doped polymers was measured at room temperature using a collinear four-probe setup DFP-2 instrument. The polymers tested

TABLE I
Yield and Intrinsic Viscosities of Polyaniline Prepared in 98% and 85% Formic Acid Media^a

Sample ^b	HCOOH strength (%)	Yield (%)	Fraction of samples	Intrinsic viscosity $[\eta]$ (dL/g)
I	98	72.10	Insoluble	0.850
II	98	7.80	Soluble	0.090
III	85	70.10	Insoluble	1.012
IV	85	6.90	Soluble	0.085

^a Reaction conditions: time = 2 h, temperature = 2°C, yield = weight of polyaniline formate/weight of aniline.

^b Samples I and II represent the precipitated and dissolved part of the polymer in 98% formic acid, samples III and IV represent the precipitated and dissolved part of polymer in 85% formic acid, respectively.

were in the form of compact disk pellets 12.7 mm in diameter and about 0.5 mm in thickness. A transmission electron microscope (Model JEM-200 CX; JEOL, Tokyo, Japan) was used to determine the particle size of the soluble polyaniline present in the polymerizing system when aniline was polymerized in 98% formic acid. The soluble fraction was sufficiently diluted with formic acid, dispersed by sonication in an ultrasonic bath for 5 min, and then deposited onto a carbon grid and stained with uranylacetate before being photographed. XRD profiles of polymer samples were recorded on a Philips (The Netherlands) PW 1700 X-ray diffractometer using Cu-K_α radiation of wavelength 1.54 Å. The range was 10–70°.

RESULTS AND DISCUSSION

Effect of formic acid strength on polymerization of aniline

It has been observed that, in the case of aniline polymerization in 98 and 85% formic acid medium more than 10% of the polymer remains soluble in the reaction mixture. The yield and intrinsic viscosity of the dissolved and precipitated part of polyaniline prepared in 98 and 85% formic acid medium are presented in Table I. The low intrinsic viscosity of the soluble part of the polymer indicates that the polymer that remains soluble in formic acid is of low molecular weight, presumably attributed to the dissolution in reaction mixture at an early stage of formation and restricted to further growth, whereas in the case of aniline polymerization in 50 and 20% formic acid medium, the reaction mixture does not contain an appreciable amount of soluble polyaniline.

The reaction pathway of polyaniline formation in formic acid medium

The initial reaction pathway and intermediates generated during the polymerization of aniline in dilute

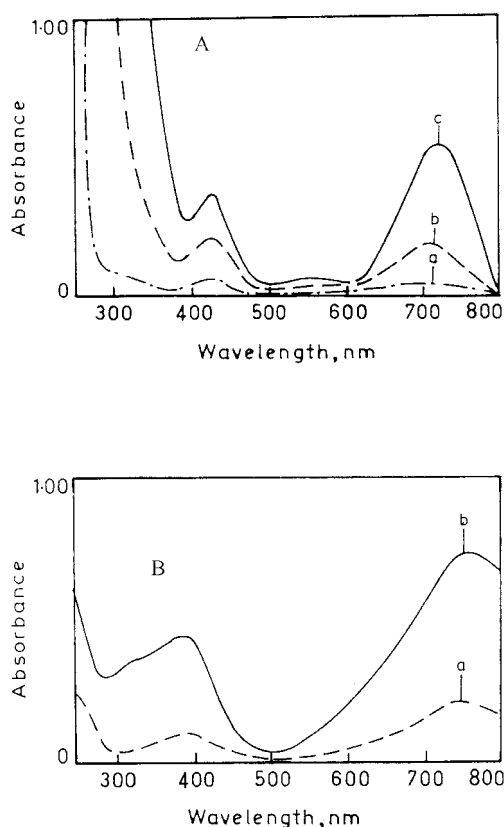
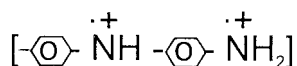


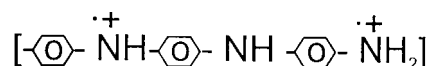
Figure 1 UV-visible spectra of reaction mixture at different times (t in min) from the initial addition of oxidant: (A) in 5.0N HCOOH [(a) $t = 8$, (b) $t = 10$; (c) $t = 14$]; (B) in 22.0N HCOOH [(a) $t = 5$, (b) $t = 8$].

[13.0N, 5.0N] and concentrated [25.0N, 22.0N] formic acid may not be identical, as indicated by the differences in color changes as well as optical spectra of the reaction medium before precipitation of the solid polymer. The reaction mixture of aniline polymerization under these concentrations of formic acid does not show any pink coloration; however, a transitory color change was observed in reactions in 1N HCl that could be attributed to the radical cation of aniline.¹² The UV-vis spectra (Fig. 1) of the reaction mixture in 13.0 and 5.0N formic acid media shows absorption bands at 720 and 424 nm. The intensity of these peaks increases with time. The appearance of an absorption band at 424 nm possibly indicates the generation of nitrenium cation ($C_6H_5NH^+$).¹³ The absorption band at 720 nm is indicative of the presence of protonated pernigraniline, the repeating unit of which is dication diradical¹⁴:



Because these intermediates are not observed in aniline polymerization in higher concentrations of for-

mic acid, where green coloration appears immediately after the addition of oxidant, it may be possible that either the lifetime of these species is exceedingly short to be visible or detected in the spectrum or they are not present at all as an intermediate. The appearance of absorption bands at 742 and 386 nm (Fig. 1) for the green solution indicates the presence of protonated aniline dimer, trimer, or other oligomers in the emeraldine oxidation state. As the reaction proceeds, they react with other radical cationic species in solution until the molecular weight increases to an extent to cause it to precipitate. It is also likely that all the propagating species, that is,



do not undergo a chain-lengthening process to an appreciable extent and remain soluble in the reaction medium in the form of oligomers, relatively lower molecular weight polymer, and presumably other reaction products that are not detectable by UV-vis spectra. The UV-vis spectra of this dissolved part of polyaniline in concentrated formic acid shows an absorption band at 760 nm, which is characteristic of the doped state and it is likely to be a charge-transfer band arising from quinone-iminium ions because the nitrogen quinone groups are protonated in acid medium.^{15,16} This is quite important because it clearly shows that the acid form of this aniline polymer is soluble in formic acid.

Transmission electron microscopy (TEM)

A TEM micrograph of PANI colloid prepared in 98% HCOOH, diluted, and redispersed in HCOOH (98%) by agitating in an ultrasonic bath for 5 min is shown in Figure 2. The micrographs show a wide distribution of spherical particles of different diameters in the range 20–200 nm.

Previous TEM studies of PANI show fibrillar morphology, prepared in the presence of functionalized protonic acid such as dodecylbenzenesulfonic acid (DBSA)¹⁷ and spherical, rice grain, or needle-shape morphology prepared in the presence of a soluble polymeric "steric stabilizer."¹⁸ TEM micrographs of stable dispersions of PANI produced by dispersion polymerization show particles of various sizes (30–200 nm) depending on the combination of reagent and processing conditions and can be disintegrated into particulates (<20 nm) on the application of ultrasound.¹⁹

Solubility

The base form of the dissolved part of the polymer prepared in concentrated HCOOH (25.0N, 22.0N) was

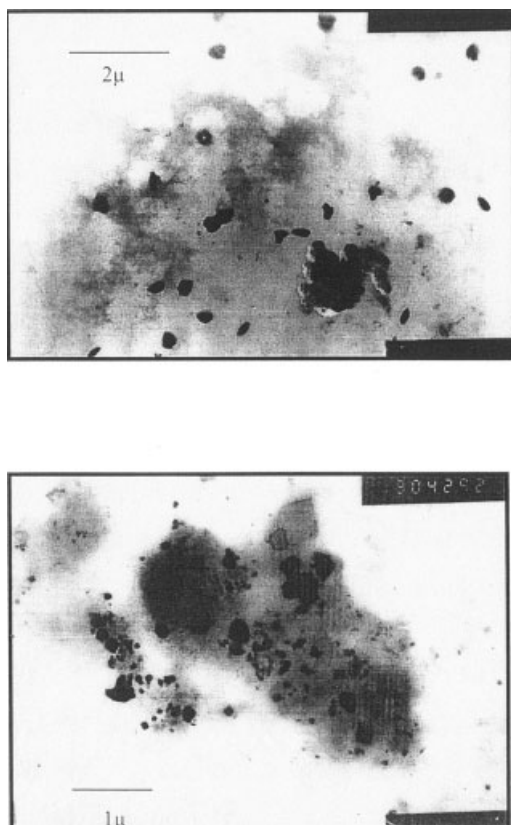


Figure 2 Transmission electron micrograph of soluble polyaniline particles prepared in HCOOH (25.0N) after sonication for 5 min.

completely soluble in DMSO, DMF, and NMP, whereas the base form of the precipitated part of the polymer prepared in both dilute and concentrated HCOOH was partly soluble in DMSO, DMF, and NMP and completely soluble in 98 and 85% HCOOH and concentrated H_2SO_4 . However, PANI-HCOOH salt remained insoluble in organic solvents.

Effect of reaction parameters

The reaction parameters such as acid concentration, temperature, time, and oxidant concentration, for example, have a great influence on the rate of oxidative chemical polymerization of aniline. They also affect intrinsic viscosity of the polymers as well as their molecular weights.

Reaction time

The effect of reaction time on yield (weight of polyaniline-formate/weight of aniline), intrinsic viscosity, and electrical conductivity of polyaniline prepared in HCOOH remains almost constant after 2 h [Fig. 3(a); Table II]. From the results, it can be seen that the maximum yield of the polymer is around 75% even

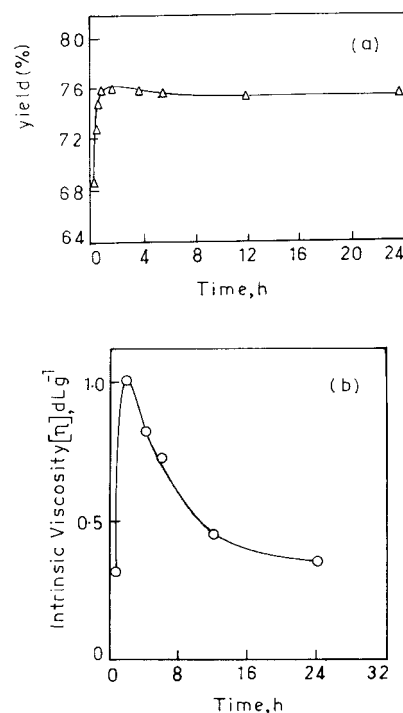


Figure 3 Effect of reaction time on (a) yield (%) and (b) intrinsic viscosity.

after 24 h of reaction time. The intrinsic viscosity of the polymer continues to increase up to 2 h then decreases [Fig. 3(b)]. There is a slight increase in electrical conductivity up to 4 h, which decreases thereafter. Conflicting reports are available in the literature as to the time of attainment of highest molecular weight of the polymer. MacDiarmid et al.²⁰ found a reaction time of 1 h to achieve maximum molecular weight and yield. However, Cao et al.²¹ found that a reaction time of 4 h is required to attain polyaniline of high molecular weight and prolonged reaction time results in a de-

TABLE II
Effect of Reaction Time on Yield, Intrinsic Viscosity, and Electrical Conductivity of the Polymer^a

Time (h)	Yield (%)	Intrinsic viscosity $[\eta]$ (dL/g)	Conductivity of the asynthesized polymer $\sigma \times 10^2$ (S cm ⁻¹)
0.33	68.9	—	—
0.50	73.2	—	—
0.75	75.0	—	—
1.00	76.0	0.320	2.1
2.00	76.3	1.012	2.0
4.00	75.1	0.822	2.5
6.00	75.4	0.745	2.2
12.00	73.9	0.455	1.8
24.00	74.2	0.366	2.0

^a Reaction conditions: formic acid concentration = 22.1N, temperature = 2°C, mole ratio of aniline to oxidant = 1, yield = weight of polyaniline formate/weight of aniline.

TABLE III
Effect of Reaction Temperature on Yield, Intrinsic Viscosity, and Electrical Conductivity of the Polymer^a

Temperature (°C)	Yield (%)	Intrinsic viscosity [η] (dL/g)	Conductivity of the as-synthesized polymer $\sigma \times 10^2$ (S cm ⁻¹)
2	76.3	1.012	2.0
10	78.5	0.622	2.9
25	78.1	0.356	2.4
35	77.3	0.162	2.1

^a Reaction conditions: formic acid concentration = 22.0N, time = 2 h, mole ratio of aniline to oxidant = 1, yield = weight of polyaniline formate/weight of aniline.

crease in viscosity of the polymer. This observation has been explained by the fact that prolonged periods seems to lead to slow hydrolysis resulting in a decrease of viscosity. However, it seems quite unlikely that dilute HCl can cause hydrolysis of polyaniline at 0°C in 24 h even in the presence of residual oxidant as concentrated H₂SO₄ (~ 36N) does not cause hydrolysis of polyaniline at 0°C in 24 h even at about 25°C (cf. viscosity measurement of polyaniline carried out in concentrated H₂SO₄).

Therefore, we consider two other possibilities to explain the decrease in intrinsic viscosity of the polymer with time. In the first case, it may be possible that the low molecular weight polyaniline (~ 10% of the total yield), which initially remains soluble in formic acid, just precipitates out with time leaving a mixture of relatively higher molecular weight and lower molecular weight polymers and thereby decreasing the intrinsic viscosity. However, this argument cannot be justified because this would result in a higher yield of polymer with time, which is really not observed. This leaves one with only presuming that with time the degree of protonation gradually increases. The intrinsic viscosity values thus do not have the same significance as the original one and cannot be directly compared. This approach stems from the fact that ESCA

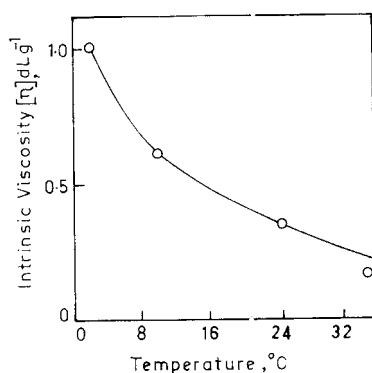


Figure 4 Effect of reaction temperature on intrinsic viscosity.

TABLE IV
Effect of Aniline to Oxidant Mole Ratio on Yield, Intrinsic Viscosity, and Electrical Conductivity of the Polymer^a

Mole ratio of aniline to oxidant	Yield (%)	Intrinsic viscosity [η] (dL/g)	Conductivity of the as-synthesized polymer $\sigma \times 10^2$ (S cm ⁻¹)
0.50	35.0	0.650	2.5
0.67	68.8	0.790	1.6
1.00	76.3	1.012	2.0
2.00	42.5	0.590	2.4
4.00	12.9	0.354	2.6
8.00	8.2	0.288	2.0

^a Reaction conditions: formic acid concentration = 22.0N, time = 2 h, temperature = 2°C, yield = weight of polyaniline formate/weight of aniline.

studies of the polymer obtained in 1M HCl at 2°C after 2 h have shown only about 20% protonation.²²

Temperature

An increase in temperature of the reaction does not show any significant effect on yield and electrical conductivity of the polymer (Table III). This is quite likely, given that the maximum yield has already been obtained at 2°C and no further changes are likely to occur at higher temperature. However, there is an appreciable change in intrinsic viscosity of the polymer with increasing temperature (Fig. 4). The electrical conductivity of the polymer does not show significant change with variation in reaction time and temperature.

Oxidant concentration

The effect of oxidant concentration on polymerization yield, intrinsic viscosity, and electrical conductivity is presented in Table IV and Figure 5, which shows the yield and viscosity as a function of the oxidant concentration. The results indicate that as the oxidant

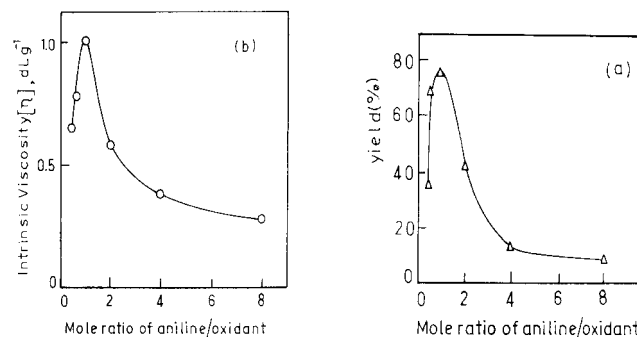


Figure 5 Effect of oxidant concentration on (a) yield (%) and (b) intrinsic viscosity.

concentration is increased above a mole ratio of 1, the yield and intrinsic viscosity are decreased. This may be attributable to overoxidation of radical cations responsible for both the growth rate and the chain length of the polymer. This is especially true in the present case because the initiating species are present in formic acid solution unlike in 1M HCl solution, when formation of byproducts is the preferred reaction. The yield and intrinsic viscosity are found to be highest at an oxidant concentration equimolar to aniline. This may be explained by formation of a maximum number of anilinium radical cations, which leads to a higher growth of polymer chains and a faster rate of reaction. On the other hand, gradual lowering of the oxidant concentration leads to successive decreases in the concentration of radical cations, resulting in a lower yield of polymer and lower intrinsic viscosity. There is marginal change in electrical conductivity. The inherent conductivity of the polymers is thus found to be scarcely affected within the molecular weight range obtained in these products.

Acid concentration

The effect of acid concentration on yield, intrinsic viscosity, and electrical conductivity of the polymer is shown in Table V. Although yield and electrical conductivity of the polymer remain almost unaffected, the intrinsic viscosity of the polymer shows a slight decrease with increase in acid concentration of the reaction medium. Previous work on polymerization of aniline in HCl medium showed that, at pH 4, the electrical conductivity and reaction yield remained unaffected, whereas the viscosity was significantly dependent on the acidity. This was explained on the basis of high acidity-accelerated hydrolysis of the emeraldine chain. The dependency of the molecular weight of polyaniline on the acidity of the reaction medium indicated that two competing processes (polymerization and degradation attributed to hydrolysis) controlled the polyaniline synthesis.²¹

TABLE V
Effect of Formic Acid Concentration on Yield, Intrinsic Viscosity, and Electrical Conductivity of the Polymer^a

Formic acid concentration (N)	Yield (%)	Intrinsic viscosity [η] (dL/g)	Conductivity of the as-synthesized polymer $\sigma \times 10^2$ (S cm ⁻¹)
25.0	76.8	0.854	3.7
22.0	76.3	1.012	2.0
13.0	77.5	1.100	2.4
5.0	78.5	1.080	2.0

^a Reaction conditions: time = 2 h, temperature = 2°C, mole ratio of aniline to oxidant = 1, yield = weight of polyaniline formate/weight of aniline.

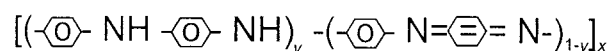
TABLE VI
Elemental Analysis of Polyaniline Salt and Its Corresponding Base Form Prepared in 85% Formic Acid

System	%C	%H	%N	Formic acid unit present per four-unit polymer chain (n)
PANI-HCOOH salt	62.83	4.67	11.37	2.2
Theoretical	63.67	4.69	11.42	2.2
Base form	78.95	4.71	14.99	—
Theoretical	79.55	4.97	15.40	—

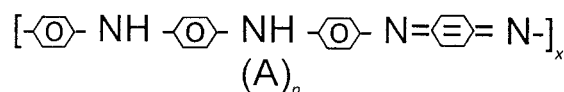
Characterization

Elemental analysis

The chemical composition of formic acid doped polyaniline was determined by elemental analysis. Polyaniline in its base form is known to contain two main structural units (i.e., benzenoid-diamine and quinonoid-diimine) and can be represented schematically by the following formula^{23,24}:

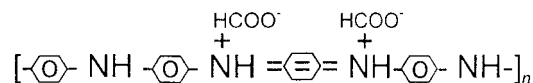


Oxidative chemical polymerization of aniline in aqueous protonic acid yields polyaniline in or close to the emeraldine form and polyaniline in its acid form may be represented by the following formula:



where A is the acid unit and n is the corresponding protonic acid unit in the polymer.

The results of elemental analysis of polyaniline-formic acid salt and its corresponding base form are shown in Table VI. It was determined that the value of n is 2.2; that is, the value of the composition of PANI-HCOOH salt is 4:2.2 and is represented by the following formula:



FTIR and UV-visible spectra

The FTIR spectra of polyaniline-formic acid salt and its base, depicted in Figure 6, show a number of vibrational bands. A band at 3300–3400 cm⁻¹ is assigned to the N—H stretching of an aromatic amine and a 2925 cm⁻¹ band to an aromatic C—H stretching. The quinonoid and benzenoid ring stretchings are present at 1563 and 1468 cm⁻¹ in the case of PANI-

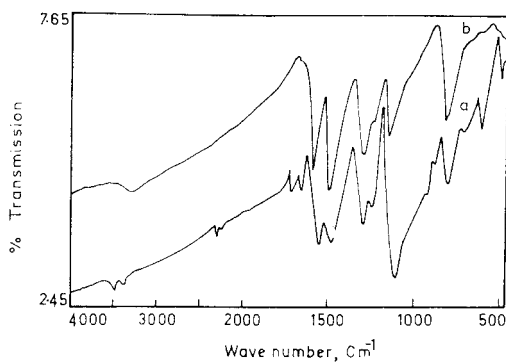


Figure 6 FTIR spectra of (a) polyaniline-formic acid salt and (b) its base form.

HCOOH salt, but at 1582 and 1488 cm^{-1} in the case of its base form. The relatively lower frequencies of quinonoid and benzenoid ring stretchings in PANI-HCOOH salt compared to that of its base form are the result of an increase in the extent of π -electron conjugation along the backbone of polymer in acid form. The appearance of a peak at 1297 cm^{-1} is assigned to C—N stretching of the secondary aromatic amine. The electronic-like absorption peak for the N=Q=N group (where Q denotes the quinonoid ring) present in base form appears at 1163 cm^{-1} .^{25,26} On doping with formic acid, the intensity of this peak increases and becomes the strongest peak in the whole spectrum, although this peak is shifted toward a lower frequency region and appears at 1108 cm^{-1} . The peak may be assigned to a mode of vibrational stretching of the B—NH—B or B—NH=Q moiety that is formed in doping reactions.^{25,26} The presence of formate anion in PANI-HCOOH salt is indicated by the appearance of peaks at 1710 and 1652 cm^{-1} for —C=O stretching that completely disappear upon basification with alkali. Appearance of the peak at 812 cm^{-1} is assigned to an aromatic C—H out-of-plane bending that may also represent the 1,4-substitution pattern of the benzene ring.

The UV-vis spectra (Fig. 7) of the base form of polyaniline prepared in 85% HCOOH in NMP shows two major absorption peaks at 624 and 321 nm. The peak at the 321-nm region is assigned to the π - π^* transition related to the extent of conjugation between adjacent phenyl rings in the polymer chain.^{26,27} The peak at 624 nm is a measure of extended conjugation, corresponding to the exciton-like transition from the highest occupied benzenoid ring to the lowest unoccupied quinoid ring caused by interchain or intrachain charge transfer.^{26,27}

Thermal analysis

The TGA thermogram of polyaniline base form prepared in 85% formic acid shows a two-step weight

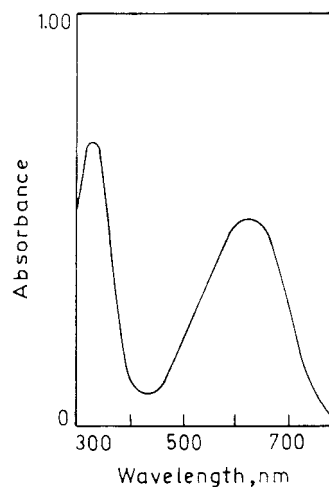


Figure 7 UV-visible spectra of the base form of polyaniline prepared in HCOOH (22.0N).

loss. In the first step, there is a 5% weight loss at a temperature around 100°C that can be attributed to the loss of moisture.^{28,29} The second step weight loss starts at 400°C and results in a 60% weight loss up to 650°C , which is attributed to thermal degradation of the polymer.³⁰ The TGA thermogram (Fig. 8) of PANI-HCOOH salt shows a three-step weight loss. The first step shows an approximately 10% weight loss at 100°C , attributed to loss of moisture and free acid present in the polymer.^{28,29} The second step shows an almost 25% weight loss that takes place continuously from 200 to 360°C , which is attributed to evolution of formic acid dopant bound to the polymer backbone.³¹ The third step shows a nearly 30% weight loss up to 650°C that can be attributed to thermal degradation of the polymer.³¹

Wide-angle x-ray diffraction (WAXD)

A WAXD powder pattern for polyaniline synthesized in 98% HCOOH is shown in Figure 9. Polyaniline

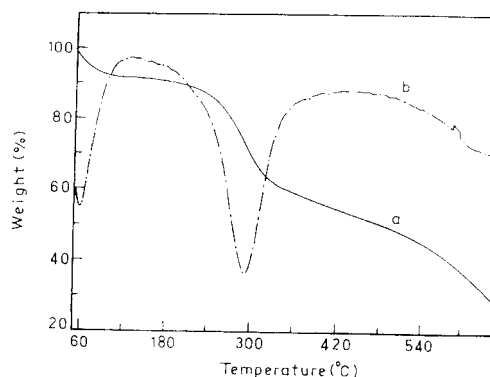


Figure 8 (a) TGA thermogram of polyaniline-formic acid salt; (b) its first derivative plot.

prepared from aqueous HCl solution in the protonated form exhibits ES-I crystal structure, which is pseudo-orthorhombic in nature with lattice parameters, $a = 4.3 \text{ \AA}$, $b = 5.9 \text{ \AA}$, $c = 9.6 \text{ \AA}$, and $v = 245 \text{ \AA}^3$.^{32,33} The d spacing corresponding to different planes was calculated from the well-known Bragg equation, $2d \sin \theta = n\lambda$, where θ is the scattering angle known as the Bragg angle. The d spacing of the Bragg reflections observed from the X-ray diffraction pattern of PANI-HCOOH salt is compatible with pseudo-orthorhombic lattice symmetry. The indexation for the reflections of largest d spacing is given in Table VII. A least-squares fit of their 2θ angular positions leads to the following pseudo-orthorhombic parameters: $a = 4.6 \text{ \AA}$, $b = 6.8 \text{ \AA}$, $c = 9.4 \text{ \AA}$, and $v = 294 \text{ \AA}^3$.

The percentage crystallinity obtained for PANI-HCOOH salt is about 26% compared to about 52% for PANI-HCl salt. The base forms of these polymers are predominantly amorphous. The degree of crystallinity is found to depend on the rigidity of the molecular chain that favors crystal packing, which in turn enhances the degree of crystallinity. In the present case, dopant anions play a significant role in increasing the percentage crystallinity of the polymer starting from amorphous bases. The crystallinity of polyaniline decreases with change in dopant anion, that is, chloride to formate.

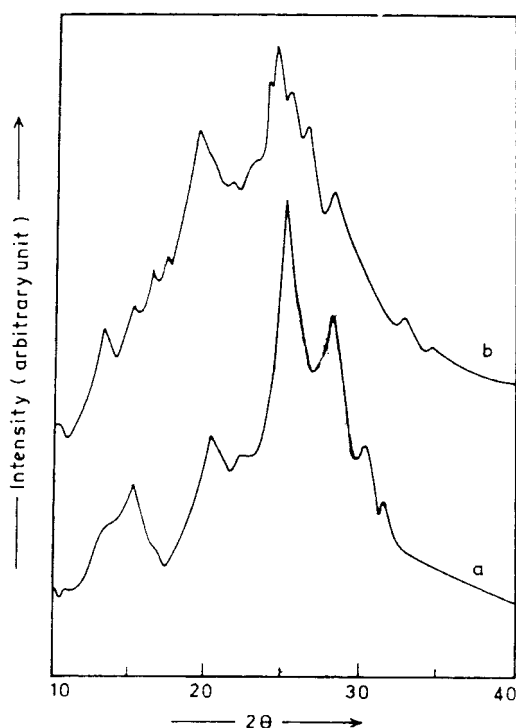


Figure 9 Wide-angle X-ray diffraction patterns for (a) polyaniline-HCl salt and (b) polyaniline-HCOOH salt.

TABLE VII
Bragg's Angle (2θ), d Spacing, Intensity, and (hkl)
Indexation of PANI-HCOOH Salt

2θ ($^\circ$)	d (\AA)	Intensity ^a	(hkl)
13.02	6.79	m	(010)
19.36	4.58	s	(100)
24.26	3.66	s	(110)
25.25	3.52	m	(111)
26.20	3.39	w	(020)
28.00	3.18	w	(021)

^a s, strong; m, medium; w = weak.

CONCLUSIONS

We investigated the oxidative polymerization of aniline in formic acid of various concentrations. The UV-visible absorption spectra of the reaction mixtures indicate that the initial reaction pathways and intermediates are dependent on the acid concentration. The polymerization rate increases with increasing acid concentration as indicated by immediate appearance of green coloration of the reaction mixture in 25.0N HCOOH just after the addition of oxidant. This results in the formation of low molecular weight polymer that remains soluble in reaction mixture. A transmission electron micrograph of the dissolved part of polyaniline prepared in 98% HCOOH shows a wide distribution of spherical particles of diameter in the range 20–200 nm. The relationships between the chemical polymerization conditions and the physicochemical properties of polyaniline prepared in 22.0N HCOOH were also studied. It was found that the electrical conductivity of the polymer remains almost unaffected by most of the reaction variables, whereas the viscosity or molecular weight and reaction yield were found to be significantly affected. Structural characterization of PANI-HCOOH salt by elemental analysis shows that its chemical composition is 4 : 2.2, which indicates two units of formate anions present per four-unit polymer chain containing a 3 : 1 ratio of benzenoid to quinonoid moieties. The presence of formate anion in polyaniline-formic acid salt is indicated by the appearance of peaks at 1710 and 1652 cm^{-1} for C=O stretching in the FTIR spectra of the polymer that completely disappear upon basification with alkali. Both FTIR and UV-visible spectra show that the polymer prepared is in an emeraldine oxidation state. TGA analysis of the polymer shows that the base form is stable up to 400°C and its acid form shows about 25% weight loss in the temperature range $200\text{--}300^\circ\text{C}$, indicating evolution of formic acid dopant bound to the polymer backbone. A WAXD study of PANI-HCOOH salt shows pseudo-orthorhombic crystal structure and the degree of crystallinity is about 26% compared to the amorphous nature of its dedoped form.

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