# Potassium Iodate–Initiated Polymerization of Aniline

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**ABSTRACT:** Potassium iodate–initiated polymerization of aniline was carried out in an acidified aqueous medium in the presence and in the absence of sodium thiosulfate salt. The nature of the polyaniline (PANI) produced depended on the aniline/potassium iodate (A/PI) mole ratio. Green emeraldine salt (ES) and blue pernigraniline salt (PS) were produced at A/PI mole ratios greater than 2 and less than 2, respectively. The sodium thiosulfate salt played a significant role in the purification and properties of PANI. The optimum aniline-to-oxidant mole ratio was found to be 2 : 1. Spectral, thermal, and electrical characteristics and viscosity of the materials were studied and compared with the results. A reaction scheme has been proposed to elucidate the role of iodine(V). Sodium thiosulfate makes it easier for iodine to be separated from a system and increases the conductivity of the products. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1626–1631, 2007

**Key words:** conducting polymer; initiator; UV-vis spectroscopy; FTIR

## INTRODUCTION

Polyaniline (PANI) has been known as aniline black since 1834.[1] Recently, PANI has attracted considerable attention because of its environmental stability and its potential use in various applications[2] such as batteries, sensors, electrochromic devices, capacitors, photochemical cells, and light-emitting diodes. The synthesis process and various physical properties and applications of this novel system have been extensively discussed in several recent handbooks.[3,4] The last few years have witnessed quite a number of studies on ammonium persulfate–initiated polymerization of aniline.[5–7] But very few studies on potassium dichromate– and potassium iodate–initiated polymerization of aniline have been reported.[8,9] In our previous studies,[10,11] we investigated the hall voltage of doped aniline and the role of Cr(VI) in the polymerization of aniline.

Ammonium persulfate and potassium dichromate were found to be effective initiators of the polymerization of aniline. A literature survey[8,9] revealed that potassium salts of iodate, bromate, citrate, and permanganate have shown inferior results for yield and conductivity of PANI despite their high oxidizing power. Further studies are necessary to improve their polymerization activity.

In the present work we investigated how variation in the aniline/iodate mole ratio, in thiosulfate, in pH,

and in temperature affected the properties and yield of PANI. A reaction scheme has been proposed (based on the results and analysis) to elucidate the role of iodine(V) in oxidative polymerization of aniline.

## EXPERIMENTAL

### Materials

Aniline (Merck, Mumbai, India) was purified by distillation over zinc dust. The middle fraction of the distillate was collected and stored in a refrigerator. Potassium iodate (SDS, Lab Chem. Industry, Mumbai, India), *N*-methyl-2-pyrolidone (NMP; SISCO, research laboratory Pvt. Ltd., Mumbai, India), and sodium thiosulfate (SQ, Qualigens, Mumbai, India) were used as received.

### Synthesis

The synthesis of polymer was carried out in a three-necked round-bottom flask kept at a constant temperature (0°C–30°C). First, 22.5 mL of distilled water, 20 mL of concentrated HCl, and 2.5 mL of aniline were added to the flask and stirred well. Purified $N_2$ gas was passed through the solution for half an hour. Then 25 mL of potassium iodate solution (taking the required amount of $KIO_3$) was added slowly with vigorous stirring by a magnetic stirrer. Enough distilled water was added to make a total volume of the reaction mixture of 100 mL. Half an hour after the volume was made up, 1 g of sodium thiosulfate was added. The precipitated polyaniline salt was filtered after a specified time and then washed with distilled water until a constant mass

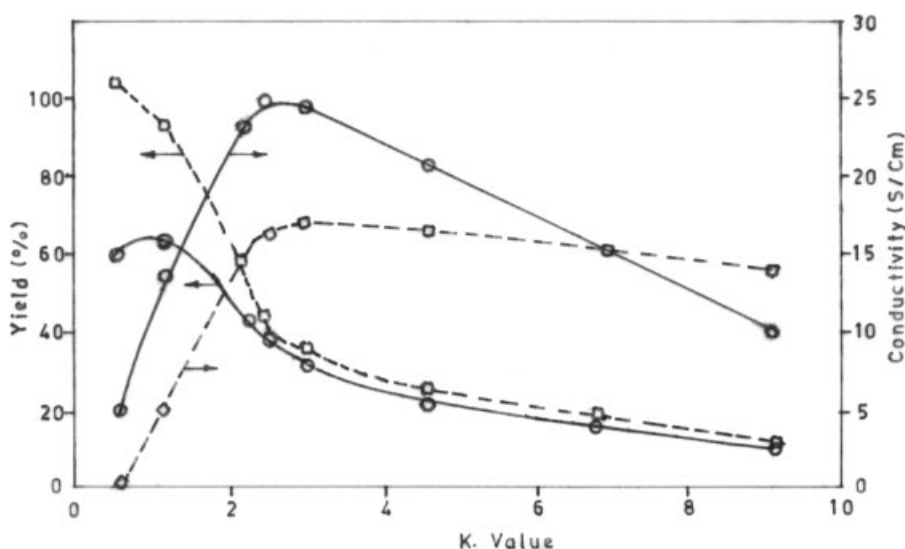*Correspondence to:* P. Chowdhury (pranesh_02@yhaoo.co.in).

**Figure 1** Variation in yield and conductivity as a function of $K$. Recipe: total volume = 100 mL, aniline = 0.027 mol, $KIO_3$ = variables, HCl = 0.2 mol, $Na_2S_2O_3$ = 0.004 mol, $T = 0°C$, $t = 4$ h. The bold line represents the system in the presence of sodium thiosulfate, whereas the dotted line represents it in the absence of thiosulfate (A/PI mole ratio = 2$K$).

was reached. The polymer yield was calculated using the relationship: yield = 100 × (amount of PANI produced)/(amount of aniline charged).

The pristine PANI salt was converted into the emeraldine base (for the UV–vis spectral study) by treatment with 3% ammonium hydroxide for 4 h.[12] The base was then washed with distilled water and dried at room temperature for 48 h under dynamic vacuum.

### Characterization

The electrical conductivity of PANI was measured by a standard four-probe method[10–11] at room temperature. The flow time of the PANI salts was determined at 27°C using an Ubbelhode viscometer. A 0.1% solution of PANI in concentrated sulfuric acid ($H_2SO_4$) was used for this purpose. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR (model 8400S) in the range of 450–4000 cm$^{-1}$ using KBr pellets. The visible spectra of the sample solution in concentrated $H_2SO_4$ and $N$-methyl-2-pyrolidone were recorded using a Shimadzu UV-VIS-NIR spectrophotometer (UV-3101 PC). Thermal degradation studies were performed under $N_2$ gas using a Shimadzu DT-30 at a heating rate of 10°C/min from room temperature to 500°C.

### RESULTS AND DISCUSSION

#### Effect of aniline (A)/potassium iodate (PI) mole ratio

The dotted line in Figure 1 indicates the effect of the A/PI mole ratio (expressed as $K$, where 2$K$ = A/PI)

on the properties of PANI in the absence of sodium thiosulfate. It is evident from Figure 1 that with an increase in the iodate level (i.e., a decrease in the A/PI ratio), the yield increased gradually to the normalized mole ratio of 5 and then increased steeply. The yield above 100% (at A/PI < 2) clearly indicated the presence of iodine in the product, as did. The reddish tint of the product was also evidence of iodine. The conductivity of the products reached its maximum (≈ 15 S/cm) at the normalized mole ratio. The highest yield (in the absence of thiosulfate) was found to be about 103% at an A/PI mole ratio of 1.7–2.

The bold line in Figure 1 reveals the effect of $Na_2S_2O_3$ on the yield and conductivity of PANI. It is evident that the yield was lower and the conductivity greater than in the system without thiosulfate. The decreased yield was a result of the removal of iodine from the product as soluble sodium tetrathionate.[13] Removable of the iodine produced increased the conductivity of PANI. In the presence of thiosulfate, conductivity was at its maximum (≈ 25 S/cm) with the normalized mole ratio. The maximum yield (in the presence of thiosulfate) was found to be approximately 65% at an A/PI mole ratio of 1.7–2.

At a mole ratio below 2, the PANI was blue in color [pernigraniline salt (PS)],[11] whereas at a mole ratio above 2, it was green [emeraldine salt (ES)].[11] The use of slightly excess iodate converted half-oxidized ES to fully oxidized PS. The decrease in yield at an A/PI ratio less than 2 was probably a result of the oxidative degradation of the polymer, although the decrease in yield with an A/PI ratio higher than 2 seems to have been a result of the
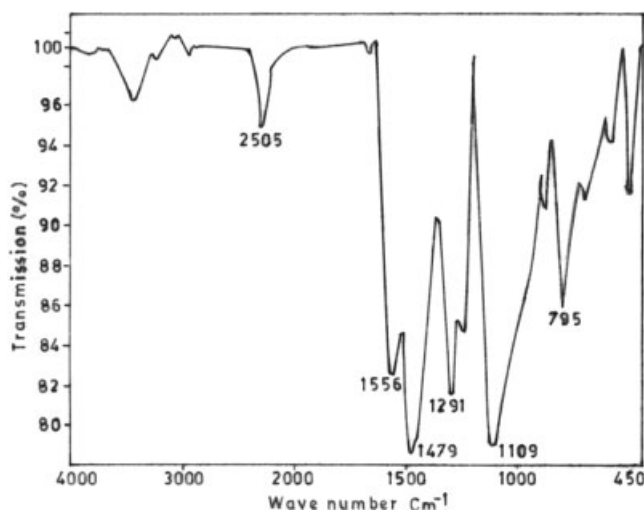
**Figure 2** FTIR spectra of PANI 1.

formation of soluble oligomer (because of a smaller amount of oxidant).

From the above discussion it may be concluded that iodine contamination of the products may be removed by using calculated amount of sodium thiosulfate at the time of polymerization. Paoli et al.[8] reported an 80% yield of PANI with a conductivity of 17–23 S/cm using $KIO_3$ (A/PI = 1.7–2.0). It seems that such a high yield was probably a result of the iodine in the product. In the same conditions, we got yields of 65% and 103% in the presence and the absence of sodium thiosulfate, respectively. The use of sodium thiosulfate gave rise to better conductivity and purity of the PANI.
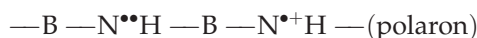
### FTIR spectral analysis

The FTIR spectrum of the PANI 1 sample (produced by using an A/PI mole ratio < 2) is shown in Figure 2. The spectrum exhibited several characteristic peaks, at 2005, 1556, 1479, 1291, 1109, and 795 cm$^{-1}$. The nature of the absorption bands and corresponding peak assignments are shown in Table I. The peak assignments revealed that the produced product was the PS form of PANI and had the following structure:

$$— B —N^{\bullet+}H —B —N^{\bullet+}H — \leftrightarrow — B —N^+H$$
$$= Q = N^+H —$$
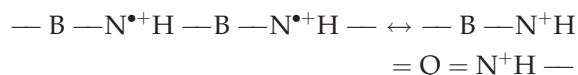
where B is the benzenoid ring and Q is the quinonoid ring.

Similarly, FTIR spectrum (not shown) of the PANI 2 sample (produced by using an A/PI mole ratio > 2) showed all the characteristic peaks of PANI except the one at 1556 cm$^{-1}$, corresponding to quinonoid ring stretching. The absence of the peak at 1556 cm$^{-1}$ indicates the dominance of the benzenoid structure in PANI 2. The peak assignments (Table I) revealed that the product was in the ES form of PANI. The structure of PANI 2 may be represented as

$$—B —N^{\bullet\bullet}H —B —N^{\bullet+}H —(polaron)$$

where B is the benzene ring.

### UV–vis spectral analysis

UV–vis spectra of PANI (aniline/iodate mole ratio = 5, K = 2.5) are shown in Figure 3. The spectrum shown in Figure 3(a) represents PANI in NMP solution, whereas that shown in Figure 3(b) represents PANI in a concentrated $H_2SO_4$ solution. The spectrum in Figure 3(a) shows two absorption maxima, at 630 and 330 nm. The $\lambda_{max}$ at 330 nm corresponded to the $\pi–\pi^*$ transition of the benzene ring,[5,16,18] and the broad absorption peak at 630 was a result of the $n–\pi^*$ transition from the nonbonding nitrogen lone pair to the conduction band.[6,16,19] The sharp peak at 630 nm indicated PANI remained in the emeraldine base form in the NMP solution.[16] Because NMP is a highly polar solvent ($\varepsilon = 32$), the solute–solvent interaction would be strong enough. The C=O group in the NMP molecule would try to form a hydrogen bond with the NH segment of the polymer chain.[16] This in turn would bring about the deprotonation of the polymer chain, resulting in conversion of the salt phase into the insulating emeraldine base

**TABLE I**
**FTIR Bands (cm$^{-1}$) of PANI**

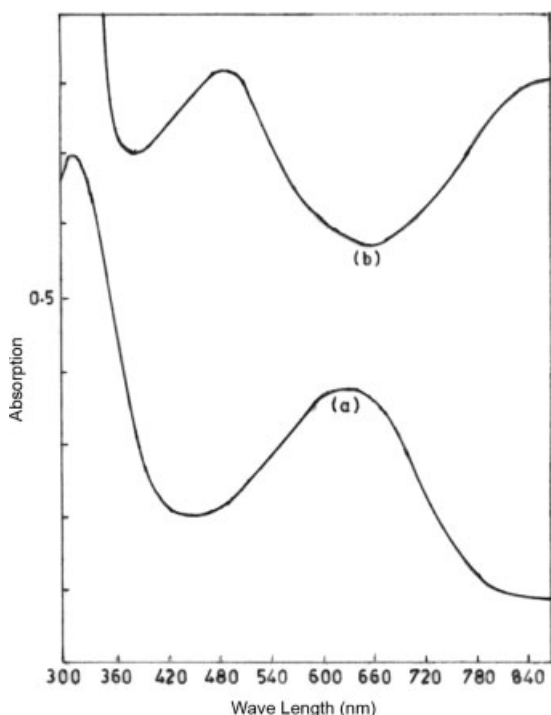| Peak position (cm$^{-1}$) | Nature of peak | Peak assignment | References |
|---|---|---|---|
| 2505 | Broad | NH$^+$ stretching of amine | 14 |
| 1556 | Shoulder | Quinoid ring stretching | 15, 25, 26 |
| 1479 | Intense and sharp | Benzenoid ring stretching | 5, 25, 26 |
| 1291 | Sharp | C—N stretching band | 16 |
| 1109 | Strong and sharp | Vibration band of dopant anion | 14, 15 |
| 795 | Sharp peak | Para-disubstituted benzene | 17, 27 |

**Figure 3** UV–vis spectra of PANI in (a) NMP solution and (b) concentrated $H_2SO_4$ solution.
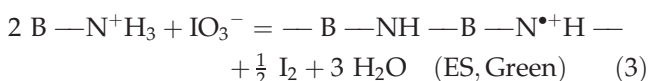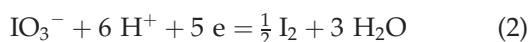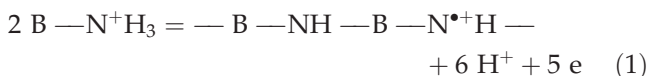
form. The absence of the extended tail at a higher wavelength ($\approx$ 800 nm) indicates the coiling up of the polymer chain.[16,20]

The spectrum shown in Figure 3(b) exhibited a sharp peak at 480 nm, and a broad band at 800 nm extended to the near-infrared region. The peaks at 480 nm could be assigned to the localized polaron, which is characteristic of a protonated polyaniline.[16] The broad band at a higher wavelength represented the extended coil conformation.[21] Thus, it may be concluded that the UV–vis spectra indicated the dominance of the polaron structure of the PANI.
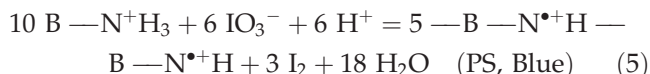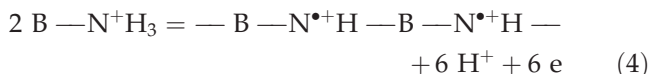
### Proposed reactions

The following reactions are proposed to explain the effect of the A/PI mole ratio and the observed color change during polymerization.

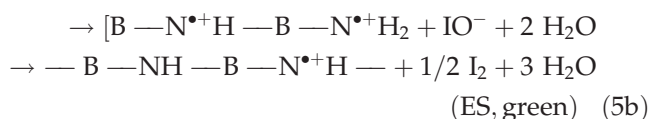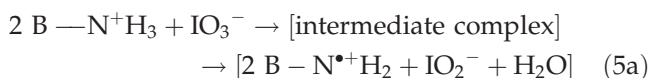**Case I**—when the A/PI mole ratio is greater than 2:

$$2 \, B\!-\!N^+H_3 = -\,B\!-\!NH\!-\!B\!-\!N^{\bullet+}H\!- \\ +\,6 \, H^+ + 5 \, e \quad (1)$$

$$IO_3^- + 6 \, H^+ + 5 \, e = \tfrac{1}{2} \, I_2 + 3 \, H_2O \quad (2)$$

$$2 \, B\!-\!N^+H_3 + IO_3^- = -\,B\!-\!NH\!-\!B\!-\!N^{\bullet+}H\!- \\ +\,\tfrac{1}{2} \, I_2 + 3 \, H_2O \quad (ES, Green) \quad (3)$$

**Case II**—when the A/I mole ratio is less than 2:

$$2 \, B\!-\!N^+H_3 = -\,B\!-\!N^{\bullet+}H\!-\!B\!-\!N^{\bullet+}H\!- \\ +\,6 \, H^+ + 6 \, e \quad (4)$$

$$10 \, B\!-\!N^+H_3 + 6 \, IO_3^- + 6 \, H^+ = 5\,-\!B\!-\!N^{\bullet+}H\!- \\ B\!-\!N^{\bullet+}H + 3 \, I_2 + 18 \, H_2O \quad (PS, Blue) \quad (5)$$

where B is the benzene ring.

### Role of iodate

The $E^\circ$ for the $IO_3^-$–$I_2$ system is lowest among halates, but iodates are kinetically the fastest to react.[13] In fact, for chlorate and bromate, the yield is very low in the same conditions. According to the literature,[13,22] during oxidation of an organic compound by iodates, the stepwise reduction of iodate is: $I^VO_3^- \rightarrow I^{III}O_2^- \rightarrow I^IO^- \rightarrow I^0_2 \rightarrow I^-$ ($IO_2^-$ is highly unstable and has only recently been identified as a transient species in aqueous solutions). During polymerization to aniline, the formation of aniline cation radicals and unstable semidine was identified as two intermediate steps.[11,23,24]

$$2 \, B\!-\!N^+H_3 + IO_3^- \rightarrow [\text{intermediate complex}] \\ \rightarrow [2 \, B - N^{\bullet+}H_2 + IO_2^- + H_2O] \quad (5a)$$

$$\rightarrow [B\!-\!N^{\bullet+}H\!-\!B\!-\!N^{\bullet+}H_2 + IO^- + 2 \, H_2O \\ \rightarrow -\,B\!-\!NH\!-\!B\!-\!N^{\bullet+}H\!- +1/2 \, I_2 + 3 \, H_2O \\ (ES, green) \quad (5b)$$

### Effects of hydrochloric acid concentration

The effects of HCl concentration on the yield and conductivity of PANI are shown in Table II. The yield increased significantly with an increase in HCl up to 2.4$M$ and then decreased gradually beyond 3.5$M$ HCl. The initial increased may be explained by eqs. (1) and (2), which indicate that a higher concentration of $[H^+]$ decreases the oxidizing power of ani-

**TABLE II**
**Effect of Protonic Acid Concentration on Yield and Conductivity of PANI**

| HCl concentration ($M$) | Yield (%) | $\delta$ (S/cm) |
| --- | --- | --- |
| 1.5 | 50.2 | 6.3 |
| 2.4 | 65.0 | 8.0 |
| 3.5 | 67.1 | 10.1 |
| 5.0 | 64.4 | 9.5 |
| 6.0 | 60.0 | 0.6 |

Reaction parameters: A/PI mole ratio = 2, sodium thiosulfate = 0.04$M$, $t$ = 4 h, $T$ = 0°C.

line salt and increases the oxidizing power of $IO_3^-$. The decrease in yield above $3.5M$ HCl may be a result of hydrolysis of polyemeraldine cations.[11] The conductivity increased with an increase in HCl up to 3.5, which was attributed to the HCl acting as a dopant.[10] At higher concentrations of HCl ($>3.5M$), the conductivity showed a decreasing trend, which may be attributed to the degradation of polymer due to hydrolysis.[9]

### Effect of polymerization time and temperature

Table III shows that the reaction yield was almost same over durations of 1–8 h. However, maximum flow time was observed at 4 h. The results indicate that polymerization occurred relatively rapidly and was essentially completed in 4 h. Prolonged reaction periods may lead to hydrolysis of emeraldine chains, which results in decreased viscosity.

No significant variation in yield within the temperature range of 0°C–30°C was found. The intrinsic viscosity of the products decreased with an increasing temperature above 0°C. Thus, it may be assumed that the viscosity average molecular weight of PANI decreased with an increase in the reaction temperature above 0°C. Electrical conductivity was found to be virtually independent of the polymerization temperature (0°C–30°C).

### Thermal properties

Thermogravimetric analyses of two representative samples, PANI 1 (A/PI mole ratio < 2) and PANI 2 (A/PI mole ratio > 2), are given in Figure 4. The mass loss of sample PANI 1 began around 50°C and continued to around 175°C, and in the next stage mass loss occurred rapidly, up to 500°C. The initial mass loss is a result of the loss of water molecules and the next stage because of oxidative degradation of polymer in air. Sample PANI 2 showed a similar type of thermal degradation. However, the mass loss up to 205°C was less than that of PANI 1, indicating PANI 2 had better stability, which may be explained by its benzenoid structure. Alternatively, inferior
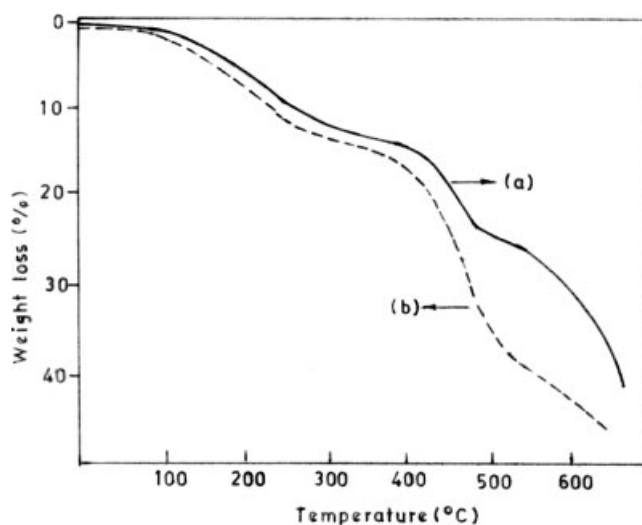


**Figure 4** TGA curves of (a) PANI 2 and (b) PANI 1.

thermal stability of PANI 1 was a result of its quinonoid structure.

### CONCLUSIONS

During oxidative polymerization of aniline by potassium iodate, the final stable form of the resulting PANI in an acid medium ($2.4M$ HCl) depended mainly on the A/PI mole ratio. A mole ratio of 2 and above led to the formation of emeraldine salt (ES), whereas that below 2 oxidized ES to pernigraniline salt. The ability of iodine(V) to oxidize aniline cations to aniline radicals through the formation of an intermediate complex makes it a successful oxidant. During oxidative polymerization of aniline, iodine(V) undergoes stepwise reduction to elemental iodine. Adding a calculated amount of sodium thiosulfate during polymerization could control iodine contamination of the products. The presence of sodium thiosulfate improved the conductivity and purity of PANI. A higher A/PI mole ratio ($>2$) led to higher thermal stability of the resulting PANI because of the dominance of the benzenoid structure.

**TABLE III**
**Effects of Polymerization Time on Properties of PANI Polymerization**

| Time (h) | Yield (%) | $\delta$ (S/cm) | $\eta_{in}$ (dL/g) |
|---|---|---|---|
| 1 | 63.5 | 7.9 | 0.75 |
| 4 | 65.0 | 8.0 | 0.78 |
| 8 | 64.5 | 7.5 | 0.63 |

A/PI mole ratio = 2, thiosulfate = $0.04M$, HCl = $2.4M$, $T = 0°C$.

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