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# Potassium dichromate initiated polymerization of aniline

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Potassium dichromate initiated polymerization of aniline in acidified aqueous medium was carried out as a function of parameters such as pH, aniline/oxidant mole ratio, temperature and time. Optimum reaction conditions are outlined for the chemical synthesis of the polymer. Spectral, thermal, electrical and viscosity properties of some selective samples of polyaniline were studied. A reaction scheme has been proposed to elucidate the role of Cr(VI).

**Keywords:** Polyaniline, dichromate oxidation, conductivity, UV-VIS spectra, FTIR spectra
**IPC Code:** C07C211/46; C08F2/00

Poly(aniline) (PANI) is known since 1862[1]. Recently this polymer has attracted considerable attention because of its environmental stability and various application potentials[2] in the areas of batteries, sensors, electro-chromic devices, capacitiors, photochemical cells and light emitting diodes. PANI is prepared by chemical or electrochemical oxidation of aniline. In chemical oxidation by strong oxidising agents in aqueous acids, PANI is obtained as insoluble fine particles[2,3]. The conductivity, yield and viscosity of PANI depend on various factors like (i) oxidising agents; (ii) aniline/oxidant mole ratio; (iii) concentration and nature of protonic acid; (iv) reaction temperature and (v) polymerization time[4-6]. The syntheses process, various physical properties and potential technological applications of this novel system have been widely discussed[7,8]. The last few years have witnessed quite good number of studies on ammonium persulphate initiated polymerization of aniline[1-6,9,10]. However, very few studies have been reported so far on the potassium dichromate initiated polymerization of aniline[4,11]. The use of $K_2Cr_2O_7$ and $(NH_4)_2S_2O_8$ resulted in high polymerization yield, electrical conductivity and viscosity[4,11] of PANI. The hall voltage and electrical resistance of doped conducting PANI has also been studied[12]. Moreover, it is noticed that the mechanism of Cr(VI) initiation in polymerising aniline has not been studied in details so far. Hence, further studies are necessary to elucidate the role of Cr(VI) in oxidative polymerization of aniline.

In the present work an attempt has been made to investigate as to how the variation of aniline/potassium dichromate mole ratio, pH, time and temperature affect the properties and yield of PANI. A reaction scheme has been proposed to elucidate the role of Cr(VI) in oxidative polymerization of aniline.

## Experimental Procedure

### Materials

Aniline (E. Merck, India) was purified by distillation over zinc dust. The middle fraction of the distillate was collected and stored in a refrigerator. Potassium dichromate (Pfizer Ltd., India) was used as received.

### Synthesis of polymer

The synthesis of polymer was carried out in a three-necked round bottom flask that was kept at a temperature (0-30°C). Small volume of distilled water, 20 mL concentrated HCl and aniline of different required volumes were taken in the flask. Purified $N_2$ gas was passed through the solution for half an hour. 25 mL potassium dichromate solution (0.44 M) was added slowly with vigorous stirring by a magnetic stirrer. The total volume of the reaction mixture was made to 100 mL by distilled water. The precipitated polyaniline salt was filtered and then washed with distilled water until the washing liquid was completely colourless. The material was dried at room temperature for 48 h in a dynamic vacuum until constant mass was reached. The polymer yield was calculated using the relationship:

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$$\text{Polymer yield} = \frac{100 \times \text{amount of PANI (g) produced}}{\text{amount of aniline (g) charged}}$$

### Characterization of PANI

The electrical conductivity of PANI was measured by a standard four-probe method[12] at room temperature. For electrical contact highly conducting graphite adhesive (Electrodag 5513 Acheson) was used. The flow time of the polyaniline salts were determined at 27°C using an Ubbelhode viscometer. 0.1% solution of PANI in concentrated $H_2SO_4$ was used for this purpose. Fourier transform infrared (FTIR) spectrum was recorded on a Perkin-Elmer Spectrum RXFTIR system in the range of 1800-450 $cm^{-1}$, using KBr pellets. Visible spectra of the samples (saturated solution in concentrated $H_2SO_4$) were recorded using Systronic digital visible spectrophotometer (Model 166). Thermal degradation studies were performed under $N_2$ using Shimadzu DT-30 at a linear heating rate of 10°C/min from room temperature to 500°C.

## Results and Discussion

### Aniline/potassium dichromate mole ratio

The effect of aniline/oxidant mole ratio on the properties of the PANI is shown in Table 1. It was found that the polymer yield, colour, electrical conductivity and flow time of the polymer solution were strongly dependent on the aniline/dichromate (A/D) mole ratio. The yield was increased with the decrease of mole ratio up to 2.4, remained unchanged up to 2.0 and then decreased with the further decrease of mole ratio. About 95.69% yield was obtained for the mole ratio from 2.0 to 2.4. Cao *et al.*[4] reported 36.9 and 83.7% yield of PANI using ammonium persulphate and potassium dichromate respectively. Rodrigues and Paoli[11] reported less than 80% yield of PANI using the same oxidants. The A/D mole ratio beyond certain range (2.0-2.4) resulted in lower final yield. The incomplete conversion of aniline to PANI due to shortage of oxidant may cause the lower yield in the case of A/D mole ratio above 2.4. In fact some soluble oligomer may be produced. By contrast, high concentration of oxidant (A/D mole ratio below 2.0) may promote the formation of low molecular weight oxidation product, which is soluble in water. Brown colouration of the product indicates the formation of oxidative products. Similar type of observation was made by Stejskal *et al*[2]. Samples PANI 6 (mole ratio 2.4) and PANI 7 (mole ratio 2.0) exhibited some distinguishing properties. The conductivity of PANI 6 was higher than that of PANI 7, probably due to their difference in structure[6,13]. The conductivity of the sample PANI 6 was 2.6 S/cm, which is comparable in magnitude to that of PANI obtained by Cao *et al*[4]. However, the conductivity value is less than that reported by Rodrigues and Paoli[11]. The yield of PANI in the present system was significantly higher than obtained by these researchers[4,11]. The colour of the samples and their corresponding $\lambda_{max}$ values indicate that PANI 6 was emeraldine salt (ES) form of polyaniline and PANI 7 was pernigraniline salt (PS) form of PANI.

The structures of PANI 6 and PANI 7 may be represented as $-B-N^{\bullet+}(H)-B-NH-B-N^{\bullet+}(H)-B-NH-$ and $-B-N^{+}H=Q=N^{+}H-B-N^{+}H=Q=N^{+}H-$ respectively (B represents benzenoid ring and Q denotes quinoid ring). The polaron form[21-25] (benzenoid structure) of PANI 6 appears to be the plausible cause of its higher conductivity.

The sample PANI 6 exhibited $\lambda_{max}$ values at 430 and 760 nm. The $\lambda_{max}$ at 430 and 760 nm are identified as higher and lower energy polaron bands caused by protonation of the imine groups of polyaniline chain[13-15]. By contrast $\lambda_{max}$ at 655 nm

Table 1—Effect of aniline/oxidant mole ratio on PANI properties
Total volume =100 mL, [HCl] = 2.4 M, [$K_2Cr_2O_7$] = 0.11 M, Temp = 0°C, Time = 4 h.

| Sample number | [ANI]/[OX] (Mole ratio) | Yield (%) | Colour $\lambda_{max}$ (nm) | Conductivity ($\sigma$) (S/cm) | Flow time (S) |
|---|---|---|---|---|---|
| PANI1 | 16 | 18.12 | Green 431,761 | 0.1 | 93 |
| PANI2 | 12 | 28.30 | Green 431,761 | 0.4 | 103 |
| PANI3 | 8 | 44.61 | Green 431,760 | 1.5 | 107 |
| PANI4 | 6 | 64.43 | Green 431,761 | 2.5 | 112 |
| PANI5 | 4 | 71.81 | Green 431,760 | 2.4 | 116 |
| PANI6 | 2.4 | 95.69 | Green 430,760 | 2.6 | 122 |
| PANI7 | 2 | 95.70 | Blue 655 | 0.9 | 123 |
| PANI8 | 1 | 63.43 | Brown | 0.7 | 99 |

indicates that the sample PANI 7 was actually pernigraniline[14].

The proposed reaction scheme reveals that A/D mole ratio for PS is 2.0 and that of 2.4 for ES. No change in yield from the mole ratio 2.0 to 2.4 may be explained on the basis of structural change (Eq. 7). The flow time reaches its maximum value within the A/D mole ratio 2.0-2.4, probably reflects full conversion of the monomer to polymer to attain maximum possible chain length or molecular mass.

The FTIR spectra of the samples PANI 6 and PANI 7 are presented in Fig. 1. The spectrum A of sample PANI 6 exhibited several characteristics peaks. The presence of strong bands at 1556 and 1480 cm$^{-1}$ are ascribed to benzenoid ring[16,17]. The spectrum B of sample PANI 7 showed sharp band at 1480 cm$^{-1}$ and no band at 1556 cm$^{-1}$. This is probably due to dominance of quinoid ring in PANI 7. Thus, FTIR data support the structures of PANI 6 and PANI 7.

The thermogravimetric analysis (TGA) of samples PANI 6 and PANI 7 are shown in Fig. 2. The mass loss of the sample PANI 7 was started at 50°C and continued up to 180°C and in the next stage the mass loss occurred rapidly up to the temperature 500°C. The initial mass loss may be due to the loss of water molecules and for the next stage due to oxidative degradation of polymer in air. The sample PANI 6 showed similar type of thermal degradation. However, mass loss up to 200°C was less than that of PANI 7, indicating better thermal stability of PANI 6.

### Effect of HCl concentration

The effect of HCl concentration on the yield and conductivity of PANI are shown in Table 2. The yield was increased significantly with the increase of HCl level up to 2.4 M, and then decreased gradually beyond 3.5 M HCl. The initial increment may be explained with the help of Eq. 8, which indicates that higher [H$^+$] concentration favours the production of ES. The decrease of yield above 3.5 M HCl may be due to hydrolysis of the polyemeraldine chains[4]. In case of $(NH_4)_2S_2O_8$ oxidation, Cao *et al.*[4] reported that the yield was unaffected with the variation of HCl concentration. It is observed from the table that the conductivity increases with the increase of HCl up to 3.5 M, which may be attributed to the fact that the HCl acts as dopant. At higher concentration [> 3.5 M HCl], the conductivity shows a decreasing trend, which may be attributed to the degradation of polymer due to hydrolysis.

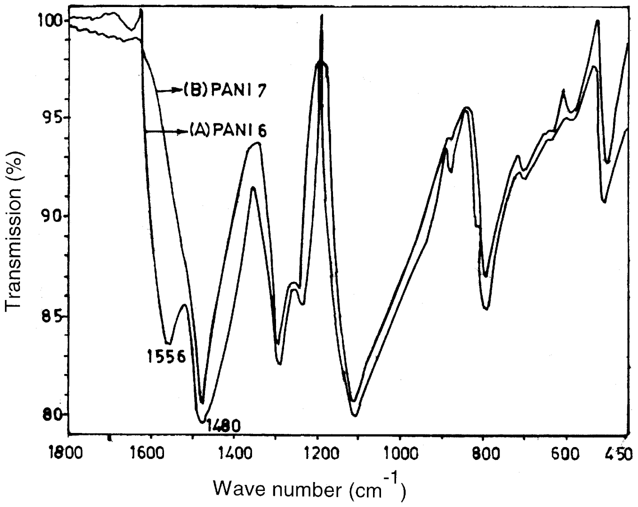


Fig. 1—FTIR spectra of PANI 6 and PANI 7

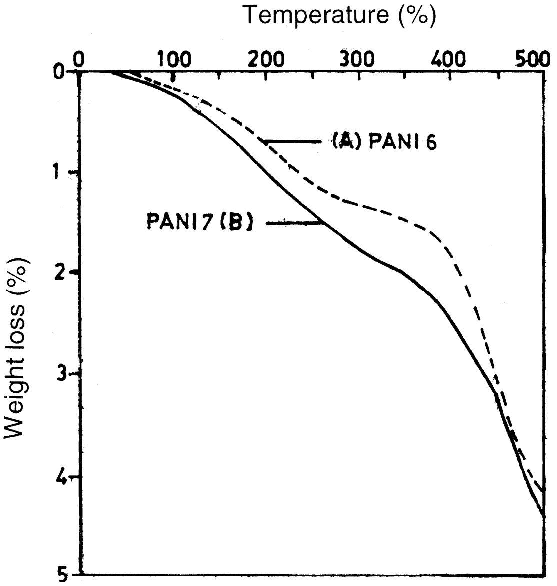


Fig. 2—TGA curves of PANI 6 and PANI 7

Table 2—Effect of protonic acid concentration on the yield and conductivity of PANI
Volume = 100 mL, $[ANI]/[K_2Cr_2O_7]$ = 2.5 (mole ratio), Temp = 0°C, Time = 4 h.

| HCl concentration (M) | Yield (%) | σ (300) (S/cm) |
|---|---|---|
| 0 | 0 | - |
| 1.5 | 65.1 | 1.2 |
| 2.4 | 95.7 | 2.6 |
| 3.5 | 97.0 | 3.6 |
| 5.0 | 94.3 | 2.9 |
| 6.0 | 93.1 | 0.9 |

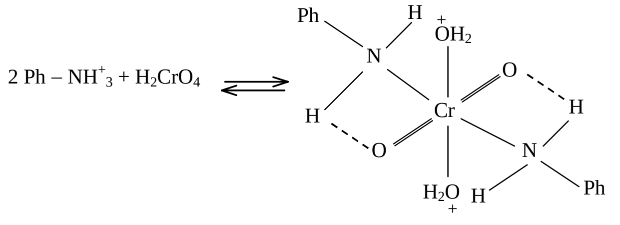
### Effect of polymerization time and temperature

Table 3 shows that the reaction yield was almost same over the periods from 1 to 8 h. However, maximum flow time was observed at 4 h. These results indicate that the polymerization occurred relatively rapidly and was essentially completed in 4 h. Prolong reaction periods may lead to hydrolysis of polyemeraldine chains, which results in decrease in viscosity. It may be mentioned that a reaction time of 1 h, which was proposed by Diarmid *et al.*[18], was not sufficient to achieve maximum molecular weight. No significant variation in yield within the temperature range 0 to 30°C, was found. Flow time of the products was found to decrease with the increasing temperature over 0°C (Table 4). Thus, it may be assumed that the viscosity average molecular weight of the PANI decreases with the increase of reaction temperature above 0°C. Electrical conductivity was found to be virtually independent of the polymerization temperature (0-30°C) (Table 4).

### Proposed reaction scheme

The following reactions are proposed to account for the colour and acidity changes observed during the oxidation of aniline.

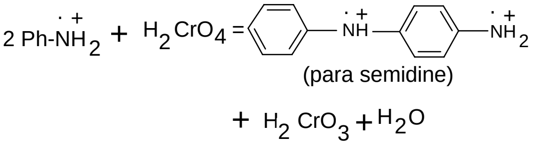
$$K_2Cr_2O_7 + H_2O + 2H^+ = 2K^+ + 2\,H_2CrO_4 \qquad \ldots(1)$$



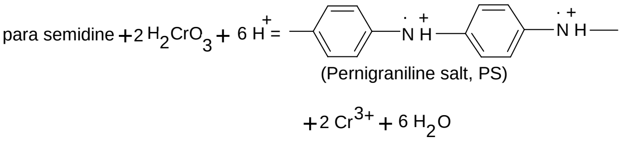
(Complex)

…(2)

$$\text{Complex} \longrightarrow 2\,\text{Ph} - \overset{\bullet +}{N}H_2 + H_2CrO_3 + H_2O \qquad \ldots(3)$$



…(4)



…(5)

Table 3—Effect of polymerization time on the properties of PANI Volume = 100 mL, [ANI]/[$K_2Cr_2O_7$] = 2.5 (mole ratio), [HCl} = 2.4 M, Temp = 0°C

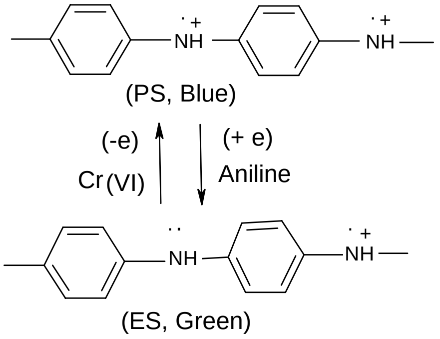
| Time (h) | Yield (%) | σ (S/cm) | Flow time (s) |
|---|---|---|---|
| 1 | 95.1 | 2.5 | 102 |
| 4 | 95.7 | 2.6 | 122 |
| 8 | 94.3 | 2.5 | 110 |

Table 4—Effect of temperature on the properties of PANI Volume = 100 mL, [ANI]/[Dichromate]=2.5 (mole ratio), [HCl]=2.4 M, Time = 4 h

| Temperature (°C) | Yield (%) | Conductivity (S/cm) | Flow time (s) |
|---|---|---|---|
| 0 | 95.7 | 2.6 | 122 |
| 15 | 95.8 | 2.6 | 119 |
| 30 | 95.6 | 2.5 | 116 |

By adding equations 1, 2, 3, 4 and 5

$$2PhNH_3^+ + K_2Cr_2O_7 + 8\,H^+ = \underset{\text{(Blue)}}{PS} + 2\,K^+ + 2\,Cr^{3+} + 7\,H_2O \qquad \ldots(6)$$



…(7)

$$12\text{ Aniline} + 5\text{ Potassium dichromate} + 34\,H^+ = 6\text{ ES} + 10\,Cr^{3+} + 10\,K^+ + 35\,H_2O \qquad \ldots(8)$$

Potassium dichromate in acidified aqueous solution produces chromic acid[19] (Eq. 1.) The chromic acid withdraws one electron from each protonated aniline and probably forms a metastable complex[20] (Eq. 2). The complex undergoes dissociation to form aniline cation radical (Eq. 3). Aniline radical plays a vital role in the preparation of PANI, as suggested by Stejskal *et al*[2]. In the case of Cr(VI) oxidation of organic compounds, it has been reported that Cr(VI) is reduced to Cr(IV) first and then to Cr(III)[20]. Transfer of two electrons from two aniline ion radical by $H_2CrO_4$ produces *N*-phenyl-*p*-phenylene-diamine (para semidine) salt (Eq. 4) along with chromous acid

($H_2Cr^{IV}O_3$). The intermediately produced Cr(IV) oxidises para semidine to pernigraniline salt (PS) at a suitable low pH (Eq. 5). As suggested by earlier authors[2,14], the PS acts as a catalyst for conversion of aniline to PANI. The Eq. 6 reveals that at the mole ratio 2 (aniline:dichromate), the colour of the solution will be blue due to the formation of PS. If A/D mole ratio is increased by adding more aniline, the obtained PANI will be in the emeraldine salt (ES) form (Eq. 7). The Eq. 8 shows that at the mole ratio 2.4, the colour of the solution will be green due to formation of ES. Excess dichromate (A/D mole ratio below 2.4) initially converts ES to PS and finally to brown coloured products.

## Conclusion

During the oxidative polymerization of aniline by potassium dichromate, the final stable form of the resulted polyaniline in acid medium (2.4 M HCl) depends solely on the aniline/dichromate mole ratio. The mole ratio 2.4 leads to emeraldine polyaniline salt while that of 2.0 oxidise to pernigraniline salt form. The ability of Cr(VI) to oxidise anilinium cation to aniline cation radical through the formation of an intermediate complex of Cr(VI), makes it successful oxidant. During aniline oxidation, Cr(VI) is reduced to Cr(IV) first by capturing two electrons and then Cr(IV) is converted to Cr(III) by withdrawing one electron from the system. In our system $K_2Cr_2O_7$ gives rise to 95% yield and conductivity to the extent of 3.6 S/cm.

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