

## Effect of Synthesis Conditions on the Morphology of Polyaniline

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Polyaniline was prepared in aqueous medium by using various synthesis conditions. The polyaniline nanoparticles were characterized in terms of their morphology, particle size, conductivity and chemical structure. The results indicate that the morphology, particle size and conductivity of nanoparticles are dependent the synthesis conditions. The chemical structure of the products was determined by FTIR spectroscopy.

**Key Words: Polyaniline, Nanoparticle, Morphology, Chemical structure.**

### INTRODUCTION

Polyaniline (PAN) is one of the most useful conducting polymers due to its ease of synthesis and environmental stability. It also has a wide range of electrical properties which can be easily controlled by changing its oxidation and protonation states<sup>1,2</sup>.

Since most of the conducting polymers are not processable, much of the efforts made in this field have been directed towards circumventing this problem. To solve this problem, various approaches have been tried, including addition of side groups to the polymer backbone<sup>3</sup>, grafting of polymers to a non-conducting polymer<sup>4</sup>, direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers<sup>5</sup> and copolymerization<sup>6</sup>.

Extensive research has been directed toward the improvement of the processability of polyaniline by copolymerization with substituted aniline<sup>7,8</sup> or doping polyaniline with stable functionalized protonic acid<sup>9,10</sup>.

Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization. Furthermore, more attention has been paid to the chemical polymerization of polyaniline which is most feasible for the production of polyaniline in large scale.

Conducting polymers have various applications such as rechargeable batteries<sup>11</sup>, electromagnetic interference (EMI) shielding<sup>12</sup>, antistatic coatings<sup>13</sup>, gas sensors<sup>14</sup>, optical devices<sup>15</sup>, removal of heavy metals from water and waste water<sup>16-18</sup>, etc.

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In this study, polyaniline nanoparticles were prepared using various synthesis conditions. Characteristics of products such as, morphology, particle size, electrical conductivity and chemical structure were studied. The results indicate that, the morphology, particle size and conductivity of product are extremely dependent on the synthesis conditions of polyaniline.

### EXPERIMENTAL

Morphologies of the products were obtained with a XL30 scanning electron microscope (SEM). Infrared spectra in the range 2500-400  $\text{cm}^{-1}$  on the polyaniline sample pellets made with KBr were measured by means of an infrared spectrophotometer (Shimadzu 4100). The room temperature conductivity of compressed polyaniline pellets were measured by a standard four-probe method using a Keithley 196 System DMM Digital Multi-meter and an Advantest R1642 programmable DC voltage/current generator as the current source.

Materials used in this work were: aniline monomer, ammonium persulfate, potassium persulfate, potassium iodate, hydroxypropylcellulose (HPC,  $M_w = 1 \times 10^6$ ), sulfuric acid and acetic acid, from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

**Polyaniline preparation:** The reaction was carried out in aqueous medium at room temperature for 5 h. Products filtered by using filter paper and then washed several times with deionized water and dried in room temperature.

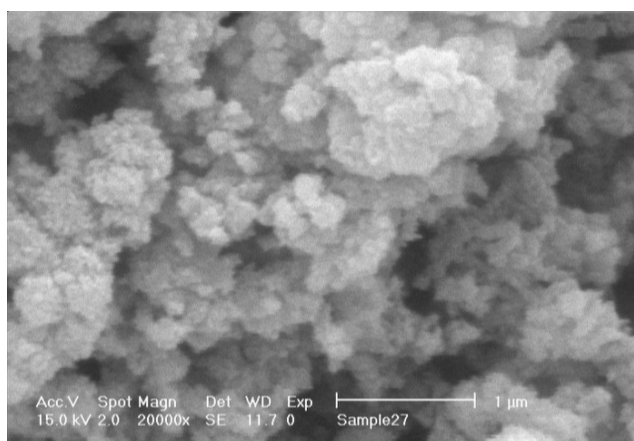
Various conditions were employed for the preparation of polyaniline: (1) 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid 1 M containing 1 g potassium iodate. (2) 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid 1 M containing 1 g potassium iodate that is at about 0 °C. (3) 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid 1 M containing 1 g potassium iodate and 0.2 g HPC. (4) 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid 1M containing 1g potassium iodate and 0.6 g HPC. (5) 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid 1 M containing 1 g potassium persulfate. (6) 2 mL aniline monomer was added to aqueous solution (100 mL) of acetic acid 0.2 M containing 5.7 g ammonium persulfate as oxidant. (7) 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid 0.5 M containing 1g potassium iodate. The details are shown in Table-1.

### RESULTS AND DISCUSSION

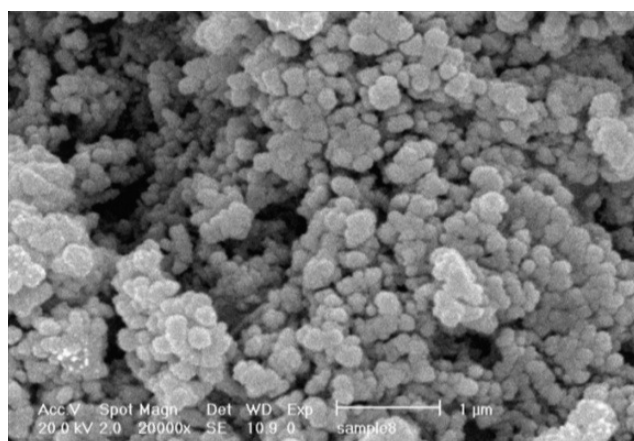
Morphology of polyaniline nanoparticles were studied, using scanning electron microscope (SEM). As shown in Figs. 1-3, the size and homogeneity of particles are dependent on synthesis conditions. These are presumably due to the physical and chemical properties of solution and rate of polymerization. Homogeneity and

TABLE-1  
SYNTHESIS CONDITIONS AND CORRESPONDING PROPERTIES OF POLYANILINE

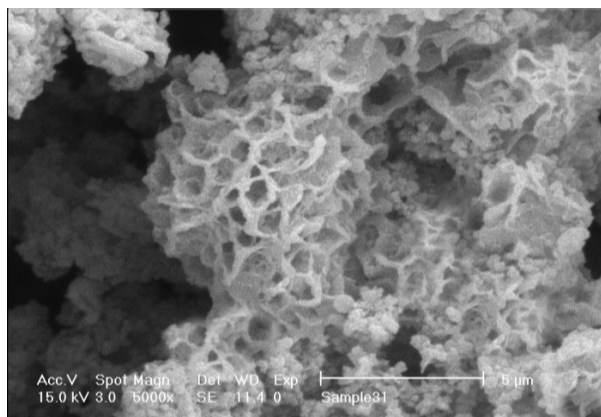
Sample No.	Solution	Aniline (mol/L) $\times 10^2$	Surfactant	Oxidant	Particle size (nm)	Conversion of monomer to polymer (%)	Electrical conductivity (S/cm)
1	H <sub>2</sub> SO <sub>4</sub> 1 M	10.75	–	KIO <sub>3</sub> 10 g/L	65	89	$1.9 \times 10^1$
2	H <sub>2</sub> SO <sub>4</sub> 1 M	10.75	–	KIO <sub>3</sub> 10 g/L	114	78	$8.6 \times 10^1$
3	H <sub>2</sub> SO <sub>4</sub> 1 M	10.75	HPC 2 g/L	KIO <sub>3</sub> 10 g/L	78	85	$4.7 \times 10^2$
4	H <sub>2</sub> SO <sub>4</sub> 1 M	10.75	HPC 6 g/L	KIO <sub>3</sub> 10 g/L	97	92	$2.8 \times 10^3$
5	H <sub>2</sub> SO <sub>4</sub> 1 M	10.75	–	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 10 g/L	D=47, L=251	85	$2.1 \times 10^1$
6	CH <sub>3</sub> COOH 0.2 M	21.50	–	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 57 g/L	D=165, L=684	93	$3.5 \times 10^1$
7	H <sub>2</sub> SO <sub>4</sub> 0.5 M	10.75	–	KIO <sub>3</sub> 10 g/L	126	93	$7.6 \times 10^3$



(a)

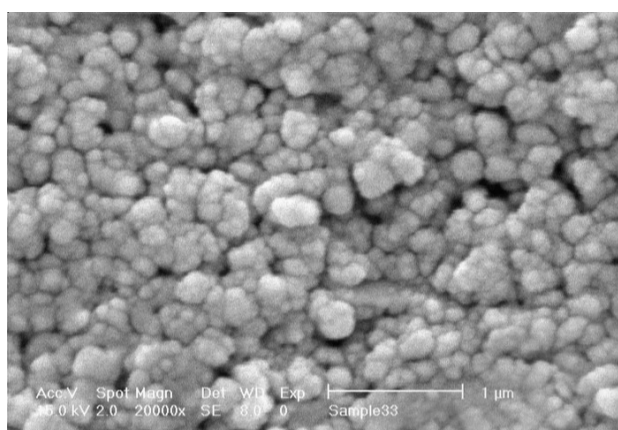


(b)

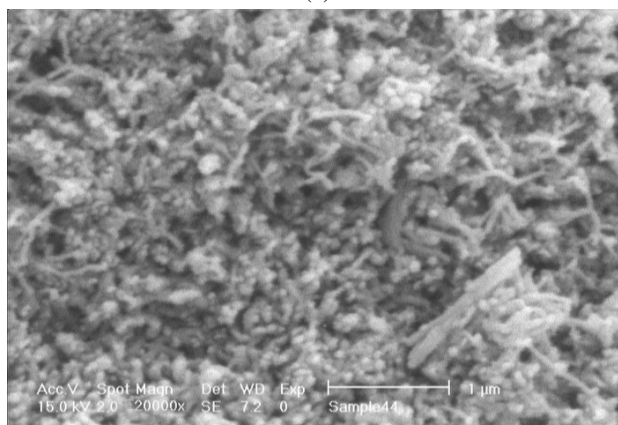


(c)

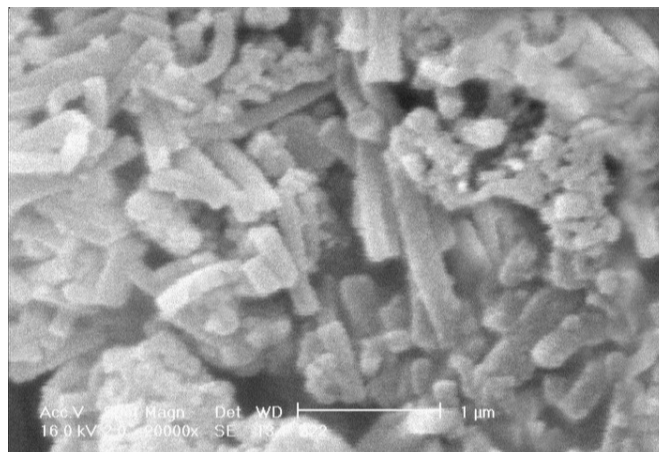
Fig. 1. Scanning electron micrograph of polyaniline. Reaction Condition: a)  $\text{KIO}_3 = 10 \text{ g/L}$ , aniline monomer  $10.75 \times 10^{-2} \text{ mol/L}$ . b)  $\text{KIO}_3 = 10 \text{ g/L}$ , aniline monomer  $10.75 \times 10^{-2} \text{ mol/L}$ , Temperature =  $0 \text{ }^\circ\text{C}$ . c)  $\text{KIO}_3 = 10 \text{ g/L}$ , aniline monomer  $10.75 \times 10^{-2} \text{ mol/L}$ , hydroxypropylcellulose =  $2 \text{ g/L}$



(a)



(b)



(c)

Fig. 2. Scanning electron micrograph of polyaniline. Reaction Condition: a)  $\text{KIO}_3 = 10 \text{ g/L}$ , aniline monomer  $10.75 \times 10^{-2} \text{ mol/L}$ , hydroxypropylcellulose = 6 g/L. b)  $\text{K}_2\text{S}_2\text{O}_8 = 10 \text{ g/L}$ , aniline monomer  $10.75 \times 10^{-2} \text{ mol/L}$ . c)  $(\text{NH}_4)_2\text{S}_2\text{O}_8 = 10 \text{ g/L}$ , aniline monomer  $2 \times 10^{-2} \text{ mol/L}$ , without stirring



Fig. 3. Scanning electron micrograph of polyaniline. Reaction Condition: Sulfuric acid 0.5 M,  $\text{KIO}_3 = 10 \text{ g/L}$ , aniline monomer  $10.75 \times 10^{-2} \text{ mol/L}$ , hydroxypropylcellulose = 6 g/L

particle size of products increased by decreasing the reaction temperature (Fig. 1a and 1b). Use of surfactant at low concentration, the morphology of product change from spherical to spongy (Fig. 1c), but at high concentration the homogeneity of spherical particles increases (Fig. 2a). Surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology and homogeneity. Adsorption of the surface active agent on the polyaniline particles is primarily due to the hydrophobic component in the surfactants, probably *via* a hydrogen bonding

mechanism with the aniline N-H group. As can be seen in Fig. 2b, using potassium persulfate as oxidant rice grain were obtained. Also when ammonium persulfate and acetic acid used as oxidant and dopant (without stirring polymerization) nanorod morphology with 684 nm length and 165 nm diameters was obtained (Fig. 2c). Finally synthesis of polyaniline in low molarity of sulfuric acid, flake particles resulted (Fig. 3).

**Structural characterization:** FTIR spectrum was used to characterize the polyaniline structure. The FTIR spectra (Fig. 4a) indicate that the polyaniline has two main peaks at 1497 and 1583  $\text{cm}^{-1}$  for the C=C stretching deformation of benzenoid and quinonoid rings, respectively<sup>19-21</sup>. The peaks at 1309  $\text{cm}^{-1}$  is assigned to C-N stretching vibration of the benzenoid ring, the peak at 1128  $\text{cm}^{-1}$  which is described by MacDiarmid *et al.*<sup>22</sup> as the 'electronic-like band' is associated with vibration mode of N=Q=N (Q refers to the quinonic-type rings) and the peak at 805  $\text{cm}^{-1}$  is attributed to the out-of-plane deformation of C-H in the *p*-disubstituted benzene ring<sup>23,24</sup>. As can be seen in Fig. 4b and 4c, these peaks shift to other number; indicating that these bands become delocalized due to use of hydroxypropylcellulose and potassium persulfate as surfactant and oxidant.

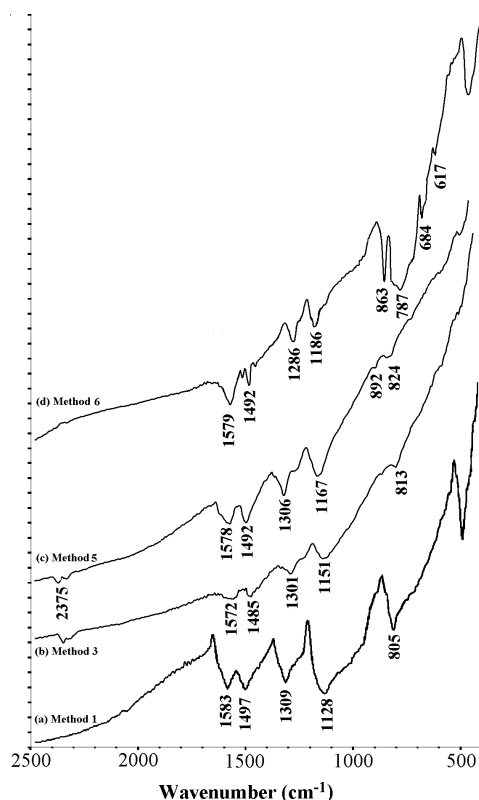


Fig. 4. FTIR spectra of polyaniline synthesized (a) method 1, (b) method 3, (c) method 5, (d) method 6

By comparison between in Fig. 4d and 4a, the chemical structure of polyaniline synthesized in acetic acid and strong acid sulfuric is different. This means that the molecular structure of polyaniline prepared under mild acidic conditions was different from that of samples prepared in solutions of strong acids. The spectrum of the polyaniline prepared in the presence of sulfuric acid is similar to that reported in the literature. The bands at 787 and 684  $\text{cm}^{-1}$  are characteristic of mono-substituted aromatic rings which are located at chain ends (Fig. 4d). This observation indicates the presence of short-chain oligomers<sup>25</sup>.

**Electrical conductivity:** The electrical conductivity of various polyaniline bases produced under different reaction conditions was measured on pressed pellets of the polyaniline powder using four point probe method. The results are shown in Table-1. As can be seen the electrical conductivity of product related to the synthesis methodology. Non ionic such as hydroxypropylcellulose decrease the conductivity of the polyaniline. Use of potassium persulfate and ammonium persulfate as oxidant, electrical conductivity of polyaniline increased because of the type of anion influence the electrical condition of product.

## Conclusion

In this work, the characteristics of polyaniline such as morphology, electrical conductivity, chemical structure and yield of monomer to polymer were investigated using various synthesis conditions. It was found that the synthesis condition has a considerable effect on the conductivity, morphology and conversion of resulting product, which is probably due to the reaction conditions influence the physical and chemical properties of solution and the rate of polymerization. As it can be seen in the micrographs, particle size and homogeneity of particles related to the synthesis condition. Also as can be seen in Fig. 4 the intensity of peaks is related to the type of synthesis method.

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