



# Synthesis Time and Temperature Effect on Polyaniline Morphology and Conductivity

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**Abstract:** This paper studies the effect of time and temperature of polymerisation on morphology and conductivity of polyaniline which is produced by oxidative polymerisation. It has been reported that with decrease in temperature and increase in polymerisation duration, the yield and particle size increases. The polyaniline particles are rod-like at the onset of polymerisation and also at low polymerisation temperature. The conductivity has been determined by four-point measurement with incorporation of correction factor. It was found that the electrical conductivity varies from below 0.5 S/cm to over 11 S/cm with variation in duration and temperature of polymerization. Conductivity is proposed to be dependent on the particle size as conductivity increases with decrease in polymerisation temperature and increase in polymerisation duration, similar to the trend observed for particle size. This may be indicative of equal probability of inter-chain and intra-chain charge transport.

**Keywords:** Polyaniline, Four-Point Conductivity, Morphology, Time Temperature Effect

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## 1. Introduction

With technological advancement and emphasis on developing flexible and wearable electronics, light-weight conducting materials are being sought. Polymers, being light weight and flexible, are an obvious choice for such applications. Some polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene and polyacetylene are known to exhibit conductivity [1, 2]. Amongst these, polyaniline offers several advantages over other conducting polymers in terms of facile synthesis, stability, morphological tunability, and control over doping level to tune conductivity [3-6].

Polyaniline is often produced by oxidative polymerisation, chemical or electrochemical, of aniline [7-9]. Standardisation of polyaniline synthesis to obtain unique electrical properties has always been a challenge and thus a vast range of conductivity values, varying from below 0.5 S/cm to over 300 S/cm, are reported in the literature [8, 10-14]. Several factors such as the choice of oxidising agent and ratio of amounts of oxidising agent and aniline, doping, polymerisation temperature and so on, have been shown to affect its conductivity and yield [4, 10-12, 14-18].

These factors have been shown not only to affect yield and conductivity but also the microstructure and morphology [4, 15, 19-21]. Polyaniline has been found to exhibit several nano-structural forms, given different synthesis conditions and parameters [5, 6, 19, 22]. Effect of parameters, such as cations, temperature of polymerization, substrate, on polyaniline morphology and molecular weight has been discussed in the previous work, but without much reference to effect on conductivity [6, 15, 19, 20, 23, 24]. Polyaniline nanostructures have attracted special attention in anticorrosion coatings, energy applications and sensors parameters [5, 6, 19, 22].

Very few reports are available on the effect of polyaniline synthesis and processing parameters on properties along with its correlation with the morphology [5, 12, 15, 25-27]. In this work, effect of polymerisation duration and temperature has been studied on morphology as well as conductivity. Polymerisation at sub-zero temperatures have shown an improvement in conductivity, be it solid state or liquid reaction medium [11, 12, 14, 21, 28, 29]. In a separate report morphology of polyaniline has been studied at low temperatures but the correlation between conductivity and morphology has not been well established. Here, the study has been carried out at three different polymerisation

temperatures and durations. Evolution of morphology with time and temperature has been reported. Low concentration of reactants has been used to minimize the effects of concentration [10].

Another important consideration in this paper is the strategy to extract the conductivity values from four-point measurement by using correction factors. Most of the literature on the conductivity of polyaniline has produced conductivity values by four-point method, but have not accounted for correction factors.

## 2. Materials

Aniline and ammonium persulfate (APS) were used to prepare polyaniline by oxidative polymerisation. The chemicals aniline monomer ( $\geq 99.5\%$  pure) and ammonium persulfate (APS,  $\geq 98.0\%$  pure) were purchased from Sigma-Aldrich, China. Hydrochloric acid was ordered from Alfa Aesar India. 0.2 M APS in water and 0.2 M aniline solution in 1M HCl were mixed in equimolar ratio. The time and temperature of polymerisation were varied as shown in the Table 1 below.

**Table 1.** List of various polyaniline samples prepared by varying polymerisation time and temperature and their names.

Time	30 min	6 hour	24 hour
Room temperature (27-28°C)	RT30m	RT06h	RT24h
Normal fridge (4°C)	NF30m	NF06h	NF24h
Deep freezer (-18°C)	DF30m	DF06h	DF24h

RT - room temperature (27-28°C)  
 NF - normal fridge (4°C)  
 DF - deep freezer (-18°C)

Fourier transform infrared spectroscopy (FTIR) was used to confirm formation of polyaniline. FTIR was performed on powders and pellets in the range  $500\text{ cm}^{-1}$  to  $4500\text{ cm}^{-1}$  on TENSORS 37 Bruker's. Scanning electron microscope was used to image the powders prepared. Samples were placed on a carbon tape and imaged on Zeiss Supra 40 FESEM at an accelerating voltage of 15kV.

Conductivity measurements were carried out using four probe technique by four probe set up (scientific equipment Roorkee). The change in voltage with change in current was measured. The powders were made into a pellet using 0.1-0.2 g of polyaniline powder pressed in a rectangular dice with dimension 5 mm by 10 mm by using pressure of one tonne/cm<sup>2</sup>. The dimensions, mass and calculated density of pellets from the various powders are listed in Table 2. Since the pellet has finite dimensions, the measurements were corrected by correction factors, which is discussed here. Resistivity of the sample may be calculated by using the following equation (1) where F is the correction factor and s is the probe distance which is 2 mm in this case. The ratio of voltage to current was calculated for several values and the average was taken for calculation of the conductivity.

$$\rho = 2\pi s F \frac{V}{I} \quad (1)$$

For the correction, three factors have been calculated for the given sample dimensions.

$$F = F1 \times F2 \times F3 \quad (2)$$

Where F1 is due to sample thickness, F2 due to lateral sample dimensions and F3 due to probe placement relative to the edges.

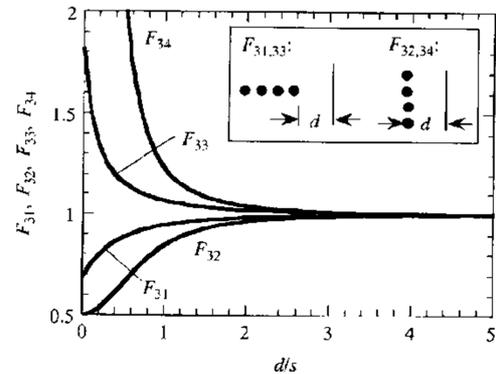
The values of F1 was calculated using equation (3) and is listed in Table 3.

$$F1 = \frac{\frac{t}{s}}{2 \ln \left[ \frac{\sinh\left(\frac{t}{s}\right)}{\sinh\left(\frac{t}{2s}\right)} \right]} \quad (3)$$

The values of F2 can be considered as 1 and F3 was found from Figure 1 [30-33].  $F_{31}$  and  $F_{32}$  represents for non-conducting bottom sample. Considering  $d/s$  as 1,  $F_{31}$  is 1 and  $d/s = 1$  for the other dimension,  $F_{32}$  is 0.8. So, taking product of the two functions, F3 was calculated to be 0.8

**Table 2.** Dimensions, mass and calculated density of pellets from the various powders.

Sample	Length (cm)	Breadth (cm)	Depth (cm)	Mass (g)	Density (g/cm <sup>3</sup> )
RT30m	0.99	0.40	0.16	0.08	1.26
NF30m	0.99	0.40	0.20	0.10	1.22
DF30m	0.99	0.40	0.21	0.10	1.23
RT06h	0.99	0.44	0.41	0.23	1.31
NF06h	1.00	0.40	0.19	0.10	1.24
DF06h	1.00	0.40	0.20	0.08	1.00
RT24h	0.99	0.40	0.33	0.17	1.28
NF24h	0.99	0.40	0.21	0.09	1.14
DF24h	1.00	0.41	0.22	0.10	1.13



**Figure 1.** Variation in values of F3 with  $d/s$  where  $d$  is distance between probe end to sample edge and  $s$  is probe spacing [30].

**Table 3.** Values of correction factors for all samples.

Sample ID	F1	F2	F3	F
RT30 m	0.53	1	0.8	0.42
NF30m	0.62	1	0.8	0.50
DF30m	0.63	1	0.8	0.50
RT06h	0.90	1	0.8	0.72
NF06h	0.60	1	0.8	0.48
DF06h	0.62	1	0.8	0.50
RT24h	0.83	1	0.8	0.66
NF24h	0.63	1	0.8	0.50
DF24h	0.65	1	0.8	0.52

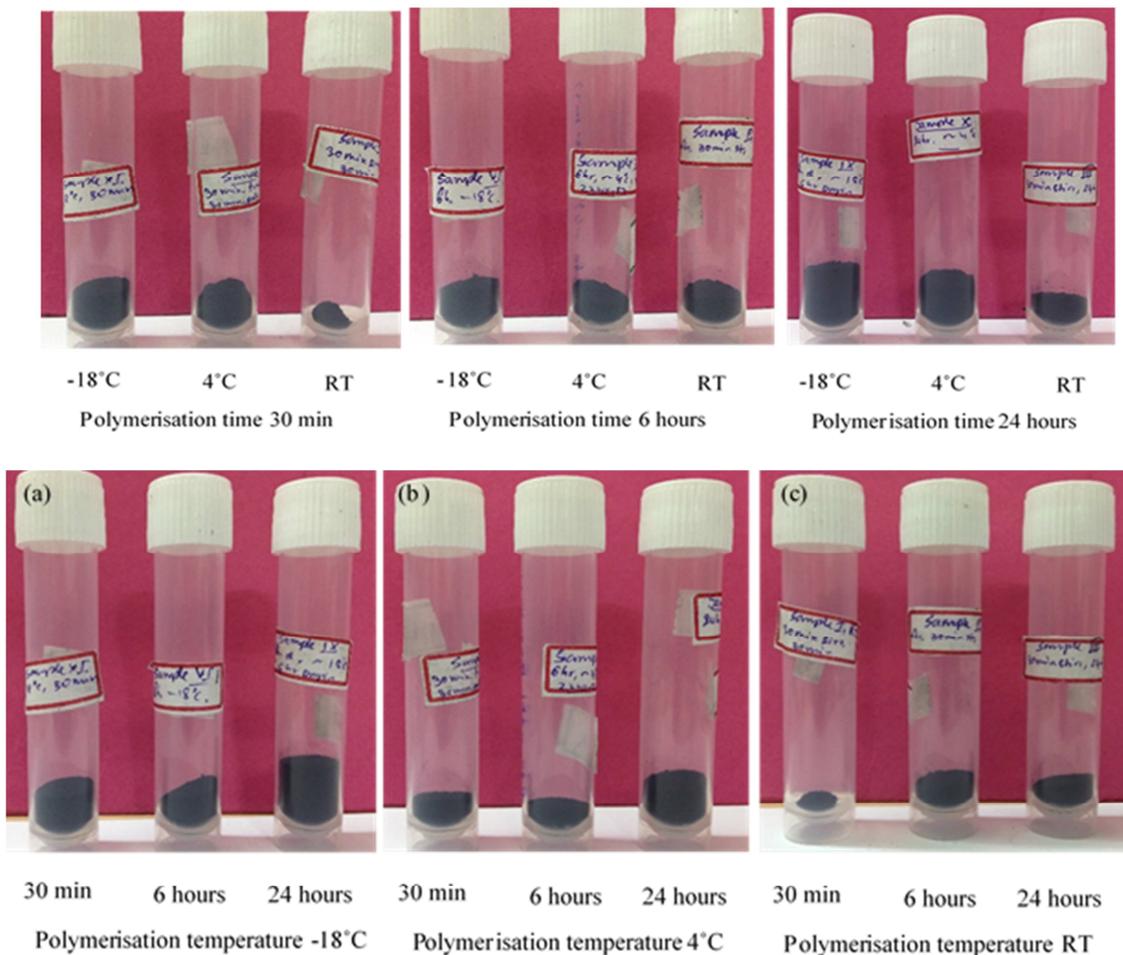
### 3. Results and Discussions

#### 3.1. Yield

Effect of time: Figure 2 (a), (b), (c) shows the powders produced at polymerisation temperatures of  $-18^{\circ}\text{C}$ ,  $4^{\circ}\text{C}$  and RT for three different durations. As the duration of polymerisation increased from 30 min to 6 hours and further to 24 hours, there is an increase in the quantity of polyaniline produced for all polymerisation temperatures. The amount of polyaniline obtained by polymerisation for 30 min at room temperature is about 0.24 g, while that for 24 hours of polymerisation, the yield is 0.32 g. The yield was 0.33 g when the polymerisation temperature was reduced to  $-18^{\circ}\text{C}$ ,

even with polymerisation duration of 30 min.

Effect of polymerization temperature: Figure 2 (d), (e), (f) shows the powders produced for polymerisation duration of 30 min, 6 hours and 24 hours, for three different polymerisation temperatures. Lower polymerisation temperature leads to higher yield. Since the polymerisation reaction is exothermic, the reactions goes forward with a decrease in temperature [34]. Therefore, larger quantity is obtained for lower temperatures of polymerisation. Also, the degradation of polyaniline, due to rise in temperature during the reaction, is expected to be lesser at lower starting temperature [10].



**Figure 2.** Powders produced at (a) polymerization temperature of  $-18^{\circ}\text{C}$  (b) polymerization temperature of  $4^{\circ}\text{C}$  (c) polymerization temperature of RT for 30 min, 6 hours and 24 hours at each temperature. Powders produced for (d) polymerization time of 30 min (e) polymerization time of 6 hours and (f) polymerization time of 24 hours at temperatures of  $-18^{\circ}\text{C}$ ,  $4^{\circ}\text{C}$  and RT.

#### 3.2. FTIR

FTIR was performed on all samples to confirm formation of polyaniline emeraldine salt. Figure 3 shows the FTIR spectra for one of samples RT24h. FTIR analysis of polyaniline emeraldine salt, the main part of the spectra has peaks corresponding to 1546, 1482, 1283, 1218, 1143 and  $764\text{ cm}^{-1}$ . Peaks at 1546 and  $1482\text{ cm}^{-1}$  are attributed to non-symmetric vibration of C-H bond in quinoid and benzenoid.

C-N bond stretching in quinoid and benzenoid are observed  $1283$  and  $1218\text{ cm}^{-1}$ . The peaks corresponding to C-H bending is seen at  $1143\text{ cm}^{-1}$ . The polar structure due to proton acid doping shows peak at  $764\text{ cm}^{-1}$ . Those values match with the literature [35, 36]. The additional peaks for C-H stretching vibration appears at  $2920\text{ cm}^{-1}$ , aliphatic hydrocarbon stretching vibration (C-H,  $\text{CH}_2$ ) at  $2838\text{ cm}^{-1}$  and that for diozonium salt at  $2377\text{ cm}^{-1}$  [26]. Therefore it can be concluded that the samples obtained are polyaniline.

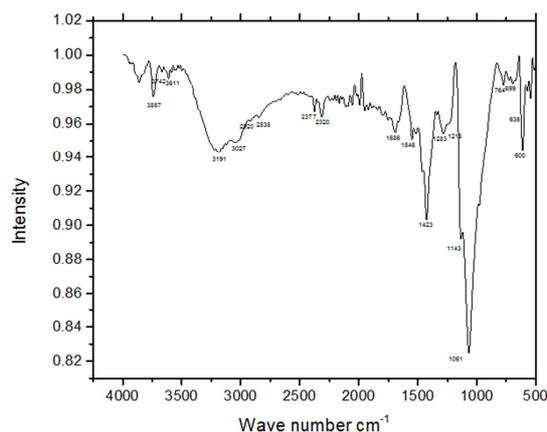


Figure 3. FTIR spectra of sample RT 24h with main peaks indicated.

### 3.3. Scanning Electron Microscopy

Figure 4 shows the SEM images of all the powders of polyaniline prepared. The average particle sizes with variation in polymerisation time and temperature are listed below in table 4. It can be seen that with increase in polymerisation duration from 30 min to 24 hours with polymerisation carried out at room temperature, particle size

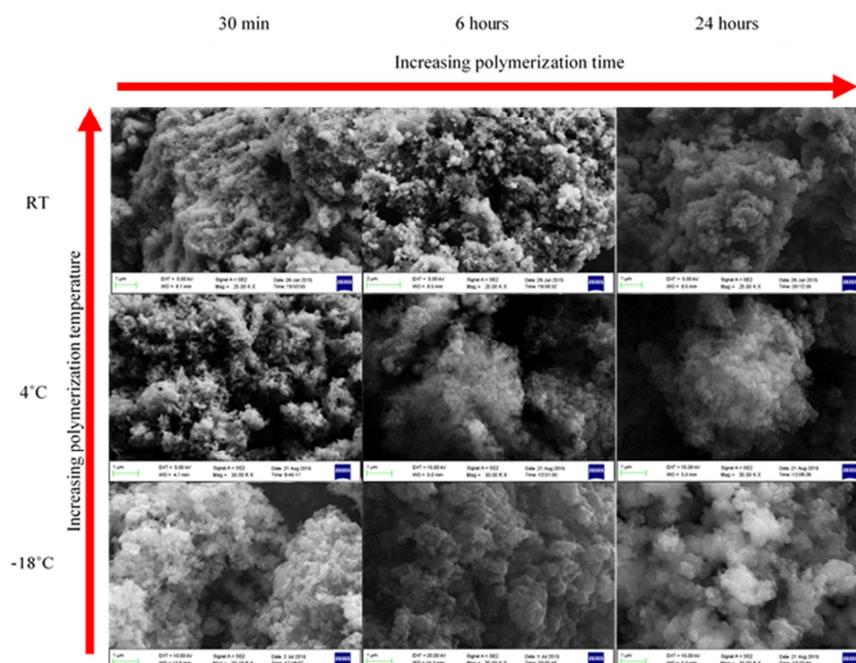


Figure 4. SEM images of polyaniline powders produced at different polymerisation temperature for different time.

Table 4. Average particle size of polyaniline produced with variation in polymerization time and temperature.

Time	30 min	6 hour	24 hour
Temperature			
Room temperature (27-28°C)	RT30m 151±47 nm	RT06h 256±70 nm	RT24h 355±81 nm
Normal fridge (4°C)	NF30m 165± 46nm	NF06h 311±75 nm	NF24h 372± 90nm
Deep freezer (-18°C)	DF30m 183±63 nm	DF06h 368± 79nm	DF24h 380±84 nm

increases from 151 nm to 355 nm and with decrease in the polymerization temperature from room temperature to -18°C, particle size increases from 151 nm to 183 nm for 30 min of polymerisation. The trends are consistent for all cases studied in this paper.

It can be seen that for 30 min polymerization time, rod-like particles are present. With increase in polymerisation duration, rod-like particle become less abundant and more spherical/globular particles are seen. Similar observation can be made with increase in temperature.

The rod or fibre like morphologies are obtained by suppressing secondary growth [37, 38]. Formation of ice, for polymerisation carried out at sub-zero temperature, causes confinement of the polymerising monomer and the oxidising agent which actually increases the local concentration. This can further accelerate the polymerisation and also causes directional polymerisation. It has been shown that PANI first forms fibres [37], however, with the progress of the polymerization, the formed fibres serve as the scaffolds for the further growth of PANI and finally develop to a particle form. Thus, a longer polymerization time favours the formation globular particles [5, 20, 38-40]. Several reports have claimed increase in molecular weight with decrease in polymerization temperature [11, 41, 42].

### 3.4. Conductivity Measurement

Conductivity measurements were done by four point measurements. However due to the limitations in the size, correction factors need to be employed to correctly estimate the value of conductivity. It must be remembered that the resistivity of the material is assumed to be uniform in the area of measurement. The corrections have been done considering a non-conducting boundary at the bottom of the

pellet.

The variation in voltage with change in current for all samples was recorded at room temperature. The average values of V/I was taken for conductivity calculation below and listed in Table 5.

**Table 5.** Values of correction factors, average V/I values, resistivity and conductivity.

	V/I	S	F	P ( $\Omega$ .cm)	$\sigma$ (S/cm)
RT30 m	4.16	0.2	0.42	2.20	0.5±0.02
NF30m	0.46	0.2	0.50	0.28	3.5±0.10
DF30m	0.39	0.2	0.50	0.24	4.1±0.11
RT06h	0.27	0.2	0.72	0.24	4.2±0.12
NF06h	0.28	0.2	0.48	0.17	6.0±0.51
DF06h	0.20	0.2	0.50	0.13	7.8±0.39
RT24h	0.21	0.2	0.66	0.18	5.7±0.09
NF24h	0.22	0.2	0.50	0.14	7.1±0.14
DF24h	0.14	0.2	0.52	0.09	11.1±0.17

It can be seen from Table 6 that conductivity increases from 0.5 S/cm to 11 S/cm with increase in polymerisation time and decrease in polymerisation temperature. The increase in conductivity here may be attributed to increase in crystallinity and molecular weight. It has been indicated in the literature that with increase in polymerisation time and decrease in polymerisation temperature, molecular weight and crystallinity increases [11, 42]. It is seen from the SEM

**Table 6.** Variations in conductivity with polymerization time and temperature.

Time	30 min	6 hour	24 hour
Temperature			
Room temperature (27-28°C)	0.5 S/cm	4.2 S/cm	5.7 S/cm
Normal fridge (4°C)	3.5 S/cm	6.0 S/cm	7.1 S/cm
Deep freezer (-18°C)	4.1 S/cm	7.8 S/cm	11.1 S/cm

## 4. Conclusions

This paper shows effect of polymerisation duration and temperature on yield, conductivity and morphology. It has been shown that with increase in polymerisation duration and decrease in polymerisation temperature, the yield and conductivity of polyaniline increases. Electron microscopy reveals that the morphology changes from rod-like particles to globular morphology on increase in time and temperature. The conductivity of polyaniline varies from 0.5 S/cm to 11.1 S/cm with increase in polymerisation time and decrease in polymerisation temperature, which can be correlated to the particle size.

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