

# Synthesis and Characterization of Nanosize Poly (p-phenylenediamine) in the presence of Benzalkonium Chloride

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## Abstract

The poly p-phenylenediamine was synthesized by oxidative chemical polymerization method in the absence and in the presence of Benzalkonium Chloride (cationic surfactant) using ferric chloride as an oxidant and hydrochloric acid as an initiator. Different concentration of the cationic surfactant was used to study their effects on the polymers. The synthesized polymers were characterized using, UV-Vis, FTIR, SEM, XRD, CV and TEM. The polymers were dissolved in DMSO, DMF, acetone and acetonitrile. The incorporation of BAC in poly p-phenylenediamine has been endorsed by FTIR analysis. It showed that amine vibration peak observed at  $1617\text{ cm}^{-1}$  was shifted to high wave number  $1620\text{ cm}^{-1}$ , which indicates the interaction between polymer and the surfactant. XRD pattern showed that the formation of nanosized (28nm). SEM analysis showed that the variation in morphology of doped polymer was predominantly dependent on the concentration of the surfactant. Cyclic voltammetric studies of BAC doped polymer exhibited one oxidation peak at 857mV and one reduction peak at -399.6 mV. Electrochemical conductivity of the surfactant doped poly p-phenylenediamine was studied by impedance spectroscopic method. TEM image showed that the formation of nano sized polymer.

**Keywords:** Poly(p-phenylenediamine), Surfactant, Cyclic voltammetry, XRD, Morphology.

## 1. Introduction

Polyaniline and its derivatives attract considerable attention in recent years due to their applications in different fields [1]. Phenylenediamines are a class of aniline derivatives having an extra -NH<sub>2</sub> group in the o-, m-, or p-positions. Poly (phenylenediamine) and its derivatives represent an important class of conducting polymers and have been attracted great

attention since their discovery, owing to their molecular spectroscopic, optical and magnetic properties [2-4]. Poly-PDs have also variety of potential applications in the fields of sensors [5-8], corrosion protection[9], nanocomposite, composite[10,11] and in the electro analytical purposes[12].

Polymeric stabilizers (surfactant) affect the polymerization condition, kinetics and also the final properties of the polymer [13,14]. Surfactants have been used as an additive in the polymerization reactions for it affects the inverse emulsion pathways and it improves the properties of the polymers with respect to conductivity, stability, solubility in organic solvents, and processibility. The presence of surfactants improves the colloidal solubility of conducting polymers in organic solvents[15-17] and, consequently, also the processibility [18,19]. The surfactant micelles control the distribution of the reactants between the micellar and aqueous phases. Mahasweta Nandi et. al., have prepared mesoporous poly(p-phenylenediamine) with anionic surfactant Sodium Dodecyl Sulphate (SDS) as a template and their porosity and magnetic property was studied [20]. D. Ichinohe et al prepared o, m, p-phenylenediamines using hydrogen peroxide as an oxidizing agent in reversed micellar systems consisting of an anionic surfactant sodium di (2-ethylhexyl)sulfosuccinate and their magnetic property has been studied [21]. In this study, PpPD-BAC was prepared in the aqueous solution by chemical oxidation method using KPS as an oxidant in the presence of various surfactant ratios. The effect of the cationic surfactant *i.e.*, BAC on the chemical polymerization of phenylenediamine (PD), at different surfactant ratios and potential windows is investigated. It is also found that electrical

conductivity of BAC doped PpPD was better than that of pure PpPD and governed by changing the concen

tration of surfactant during the polymerization of phenylenediamine.

## 2. Materials and Methods

### 2.1 CHEMICALS:

The monomer p-Phenylenediamine (pPD), Benzalkonium chloride (BAC, cationic surfactant), Ferric Chloride (oxidant) and Hydrochloric acid were purchased from Merck AR grade and used as received without further treatment.

### 2.2. Synthesis of Poly (p-phenylene diamine) with and without surfactant

Aqueous micellar dispersion was prepared by chemical oxidation method. BAC doped polymers were synthesized by keeping the concentration of the monomer (0.1 M) and the oxidant (0.1 M) constant and varying the molar ratio of BAC (below cmc). Table 1 describes the synthetic conditions of the respective samples. Polymerization was performed by the addition of ferric chloride (0.1 M) in the micellar solution and stirred for 6 hrs. The precipitated particles were collected after filtering and washing with distilled water then dried at room temperature.

**Table1. Synthetic conditions of doped and undoped PpPD**

Sample	pPD(M)	FeCl <sub>3</sub> (M)	BAC(M)
PpPD	0.1	0.1	-----
PpPD1	0.1	0.1	2x10 <sup>-2</sup>
PpPD2	0.1	0.1	1x10 <sup>-2</sup>
PpPD3	0.1	0.1	1x10 <sup>-3</sup>
PpPD4	0.1	0.1	1x10 <sup>-4</sup>

### 2.3 Characterization

FT-IR spectra (Model: SHIMADZU) of the poly(p-Phenylenediamine) samples were recorded in the frequency range of 400 to 4000 cm<sup>-1</sup>. UV-Vis spectra of the samples in DMSO were taken using JASCO-V530 dual beam spectrophotometer in the wavelength region 200 to 900 nm with a scanning speed of 400 nm/min. X-ray diffraction patterns of the polymers were obtained by employing XPERT-PRO diffractometer using CuK $\alpha$  ( $k\alpha = 1.54060$ ) radiation. The diffractometer was operated at 40 Kv and 30 mA. Powder X-ray diffraction pattern was recorded. The morphological study of the polymers were carried out using Scanning electron microscope (SEM Model: JEOL JSM 6360) operating at 25 kV. The electrochemical workstation (Model 650C), CH-Instrument Inc., TX, USA was employed for performing cyclic voltammety and impedance studies.

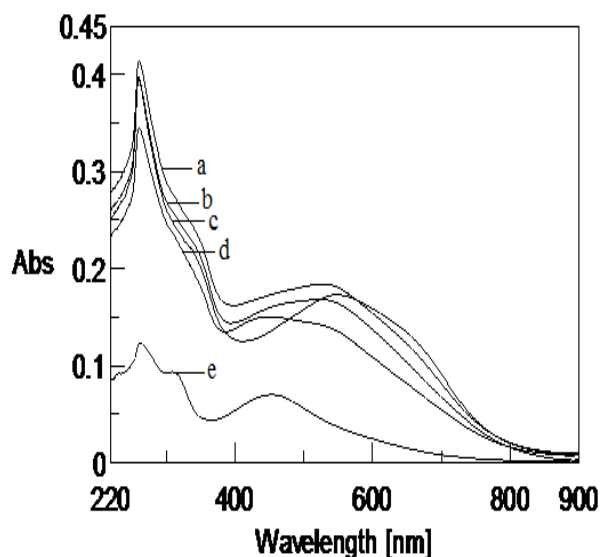
## 3. Results and Discussion

### 3.1. Solubility

The solubility of the benzalkonium chloride doped PpPD was studied in various solvents. BAC Doped PpPD was highly soluble in the solvents like DMSO, DMF, acetone, acetonitrile, ethanol, acetic acid, trichloroethylene, water and insoluble in n-hexane and benzene. This behavior was more advantage for further processing of doped PpPD.

### 3.2. UV-Vis spectra:

The UV-Vis spectrum of PpPD and BAC doped PpPD are shown in Fig.3.1. A shoulder band at around 317 nm and a strong absorption band at 262 nm are assigned to the  $\pi-\pi^*$  transitions of the benzenoid and quinoid structures of the polymer [22]. The band at 454 nm is attributed to  $\pi-\pi^*$  transition associated with the phenazine ring conjugated to the two lone pair of electrons present on the nitrogen of the NH<sub>2</sub> groups. The peaks are broad and it suggests the existence of quinine imine moieties [23]. The polymers with BAC shows similar bands corresponding to  $\pi-\pi^*$  transition of benzenoid and quinoid structures and  $\pi-\pi^*$  transition of phenazine ring and the values are shifted towards longer wavelength to some extent. By comparing the relative heights for the peaks at 262 nm and 454 nm, we can see that the band at 454 nm in the BAC doped polymer showed a higher absorption than that in the undoped polymer. This result suggests that there is an interaction between the quinoid rings of PpPD and BAC that enhance the formation of the polaron- $\pi$  transition of the polymer chain.



**Fig.3.2. UV-Vis spectra of a) PpPD 1 b) PpPD 2 c) PpPD 3 d) PpPD 4 e) PpPD (undoped)**

### 3.3. IR spectra:

The FT-IR spectra of BAC doped and undoped PpPD was shown in figure 3.2. A broad peak at around  $3414\text{ cm}^{-1}$  originates from the N-H stretching vibration of secondary amine group in the polymer chain. The peaks at  $1617$  and  $1567\text{ cm}^{-1}$  are assigned to the C=C and C=N stretching vibrations in phenazine ring. The peaks at  $1402$  and  $1288\text{ cm}^{-1}$  are associated with C-N-C stretching in the benzenoid and quinoid imine units. The peaks at  $819$  and  $601\text{ cm}^{-1}$  can be attributed to the out-of-plane bending vibrations of benzene nuclei in the phenazine skeletons [24, 25]. The strong band at around  $1169\text{ cm}^{-1}$  was supposed to be “electron-like band” which is considered to be a measure of delocalization [26]. The peaks at position  $2921$  and  $2869\text{ cm}^{-1}$  were attributed to the C-H stretching vibration of the hydrocarbon chain and the peak at  $1490\text{ cm}^{-1}$  corresponds to the C-H bending vibration of the methyl and methylene groups of the n-alkyl tail of the surfactant [27]. The PpPDA prepared with BAC have all the peaks of polymer but the values are slightly shifted towards longer wave number. The changes of peak position and intensity of IR vibrational bands confirmed the dopant in PpPD.

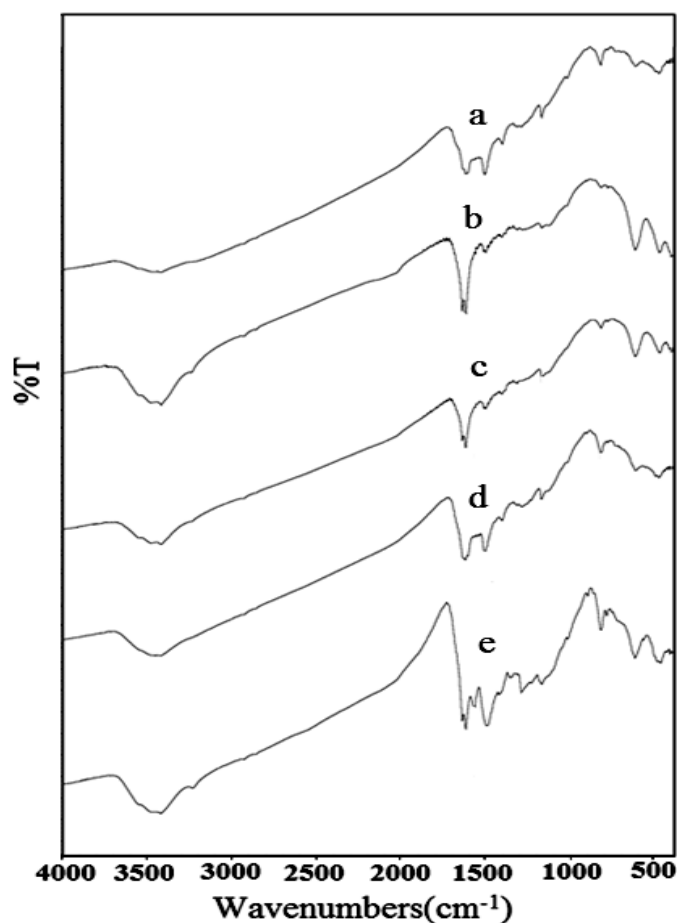
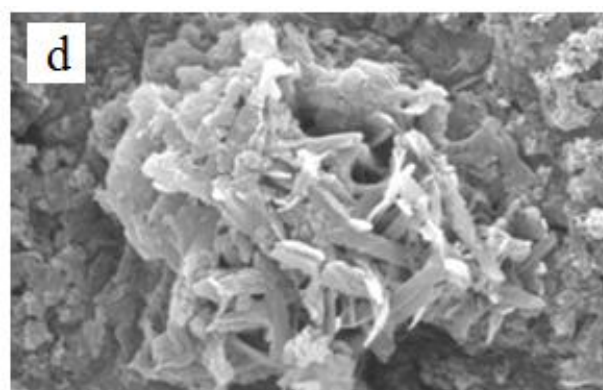
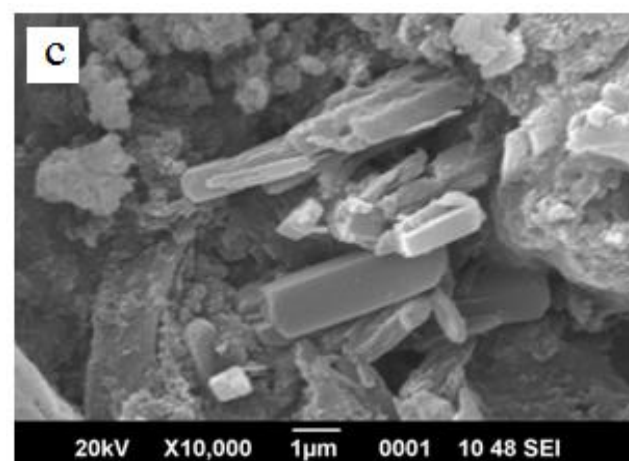
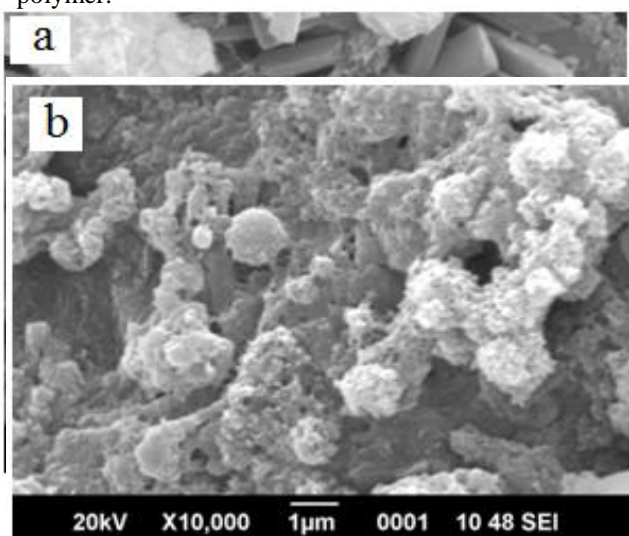
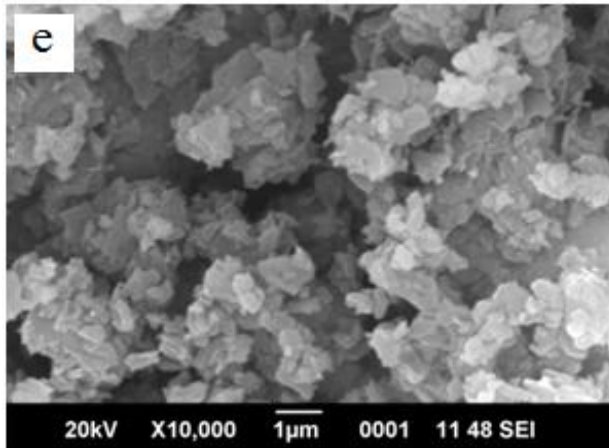


Fig.3.3. FT-IR spectra of a) PpPD 1 b) PpPDA2 c) PpPD 3 d) PpPD 4 e) PpPD (undoped)

### 3.4. SEM analysis:

The scanning Electron Microscopy (SEM) analysis was carried out to study the morphology of the polymer and polymer prepared with BAC and morphology are shown in figure 3.3. The morphology of undoped PpPD shows granular structure. The SEM image of PpPD1 (fig.3.4(a)) shows that the polymer is flakes in shape. Fig 3.4. (b&c) reveal that the marigold flowers like structure and flake like particles covered by granular structure for PpPD2 and PpPD3 respectively. PpPD4 exhibit rock like structure. The morphological changes are due to varying the mole ratio of BAC to PpPD. The dopant was confirmed by change of morphology of polymer.

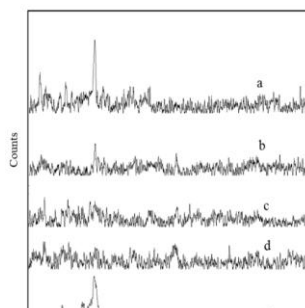




**Fig.3.3. SEM photographs of a) PpPD 1 b) PpPD 2 c) PpPDA3 d) PpPD 4 e)PpPD (undoped)**

### 3.5. XRD analysis:

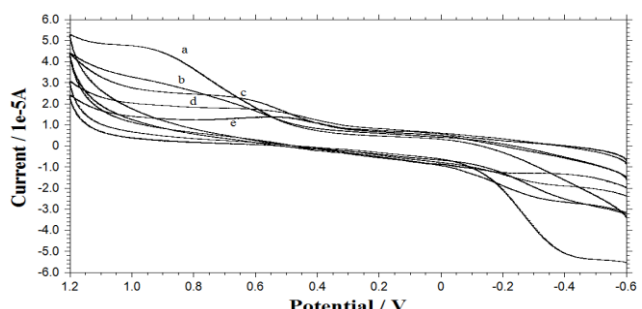
The results of x-ray diffraction are shown in Figure 3.4. XRD provide information in relation to the nature and structure of the samples. XRD patterns of undoped PpPD exhibits a broad peaks at  $2\theta=18.5^\circ$  and the size of the particle is found to be 22nm. XRD patterns of doped samples show the crystallinity. The conductivity of polymers depends on various parameters such as doping level, formation of polarons and bipolarons [28], the semi crystalline nature of polymers arises owing to the systematic alignment of polymer chain folding or by the formation of single or multiple helices, for part of their length [29]. The BAC doped PpPD exhibited sharp peak at  $2\theta = 20^\circ$  and  $26^\circ$ , this indicated the presence of a high crystallinity and condensed structure. The intensity of the peak increases with increasing the concentration of the dopant. The nanosizes of the particles were confirmed by using Debye-Scherrer's equation. The particle size varied gradually from 28nm in the case of PpPD 1 to 75nm in the case of PpPD 4 indicating that the concentration of the surfactant was highly influenced on the size of the particle. Particle size and conductivity can be decreased by increasing the concentration of stabilizer [30, 31]. The variation in diffraction intensity with dopant concentration exhibits with the interaction of BAC in the polymer.



**Fig.3.5. XRD pattern of a) PpPD 1 b) PpPD 2 c) PpPD 3 d) PpPD 4 e) PpPD (undoped)**

### 3.6. Cyclic voltammogram

Electrochemical behavior of pure PpPD and BAC doped PpPD are shown in Fig.3.5. Cyclic voltammograms were recorded at room temperature by employing a three-electrode cell with platinum wire as auxiliary electrode, an Ag/AgCl electrode as the reference electrode and coated glassy carbon (GC) as the working electrode. The CVs were obtained in 0.1 M  $H_2SO_4$  by scanned between -0.6 to 1.2 V at scan rates between 50 and 500 mV/s. The pure PpPD shows one oxidation peak at 523.2 mV and one reduction peak at -206.6 mV indicating that one redox processes are produced in the polymer [32, 33]. The BAC doped PpPD shows peaks at higher potential value (857.0 / -399.6 mV). These differences in electrochemical behavior are thought to be only to the structural differences in the PpPD systems. The higher current behavior due to fast redox process at PpPD/BAC matrix surface. The effect of scan rate variation between 25mV/s and 500mV/s was studied in 1M  $H_2SO_4$  as shown in Fig. 3.6. With an increasing scan rate the peak current also increased thus indicating good adherence of the polymer onto the GC electrode surface, the peak current separation increased, and also the peak potential shifted slightly with the anodic peak to positive and the cathodic peak to negative potential directions.



**Fig. 3.6. Cyclic voltammogram of (a) PpPD 1 (b) PpPD 2 (c) PpPD 3 (d) PpPD 4 (e) PpPD (undoped)**

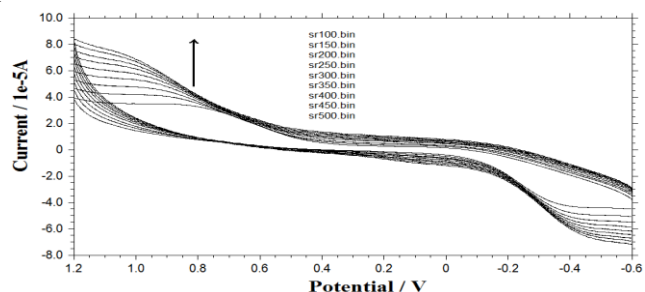


Fig. 3.7. CV taken at various scan rates for PpPD 1

### 3.7. Electro chemical Impedance Spectroscopy

Figure 3.7 shows the Nyquist impedance curves of PpPD in the presence and absence of BAC. These experimental Nyquist impedance curves were fitted well to the equivalent circuit models. The charge transfer resistance (Rct) and double layer capacitance (Cdl) of the polymers were given in the table 2. The radii of the semicircle were found to increase with decrease in the surfactant concentration. Thus PpPD 1 with maximum BAC doping shows higher conductivity.

Table 2. Impedance parameters of BAC doped and undoped PpPD

Polymers	Rct ( $\Omega \text{ cm}^2$ )	Cdl ( $\mu\text{F cm}^{-2}$ )
PpPD	3676.67	2.3718
PpPD 1	2127.66	4.5302
PpPD 2	2721.56	4.0232
PpPD 3	3191.67	3.1676
PpPD 4	3289.66	3.0102

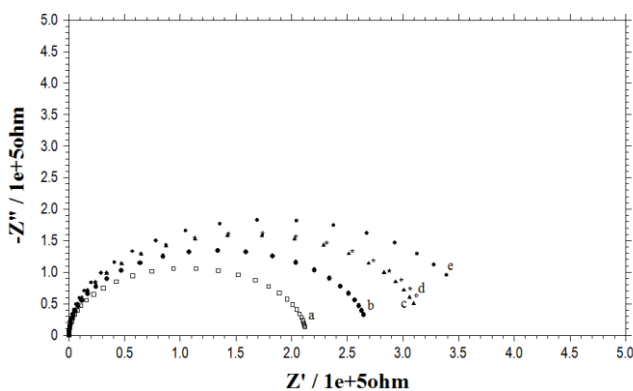


Fig. 3.7. Nyquist plots for (a) PpPD 1 (b) PpPD 2 (c) PpPD 3 (d) PpPD 4 (e) PpPD (undoped) (f) PANI (undoped).

### 3.8. TEM image:

The TEM image of the higher concentration of BAC doped PpPD is shown in Fig 3.8. The size of the particle was found to be 100nm. The morphology of the synthesized surfactant doped PpPDA was found to be nano rod like polymer. In the image, the dark portion is the surfactant and the grey areas are showing the polymer chain. Hence it is clear from the micrograph that the surfactant molecules are incorporate into the polymer.

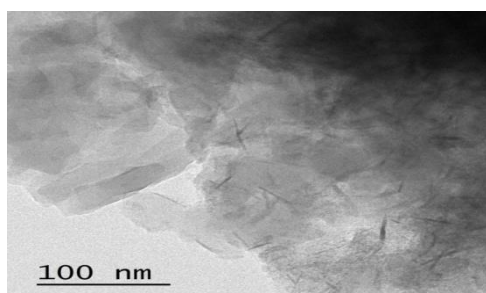


Fig.3.8.TEM image of PpPD 1

## 5. Conclusions

BAC doped PpPD was synthesized in the aqueous solution of p-phenylene diamine and cationic surfactant of benzalkonium chloride by chemical synthesis using ferric chloride as an oxidant by varying the p-phenylene diamine to BAC ratio. BAC plays as surfactant and dopant. The solubility of the polymers were ascertained and it showed good solubility in DMSO, DMF, acetone, acetonitrile, and THF. UV-Vis and FT-IR spectra confirmed the interaction of BAC in PpPD matrices. The band at 454 nm is attributed to  $\pi$ - $\pi^*$  transition associated with the phenazine ring conjugated to the two lone pair of electrons present on the nitrogen of the  $\text{NH}_2$  groups. The peaks are broad and it suggests the existence of quinine imine moieties, which is confirmed by UV-Vis spectra. The FT-IR showed that amine vibration peak observed at  $1617 \text{ cm}^{-1}$  was shifted to high wave number  $1620 \text{ cm}^{-1}$ , which indicates the interaction between polymer and the surfactant. The SEM image shows that the morphology of undoped PpPD is different from BAC doped PANI. The incorporation of BAC in PpPD matrices has different surface morphologies. XRD results show that the particle size of polymer with high concentration of the surfactant is 28 nm, while in the case of low concentration it is 75 nm. Cyclic Voltametric studies of BAC doped polymer exhibited one oxidation peak at 857mV and one reduction peak at -399.6 mV. Thus PpPD with maximum BAC doping gives maximum conductivity is confirmed by impedance spectra. TEM image confirmed the nano-sized particle.

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