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Article

Electrical Conductivity and Structural Studies on Polypyrrole Synthesized in Different Environments

Ahmad Husain, Sufiyan Ahmad, Shahid Pervez Ansari*

Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, Uttar Pradesh, India

ABSTRACT

Conducting polymers are a special class of polymers which allow electrical conductivity to pass through them. Polypyrrole is a promising conducting polymer with applications in different field of research. In this work, polypyrrole is synthesized in different environments such as variable solvent, oxidants, and oxidant ratio. The synthesized samples were collected and dried in an air oven. They were characterized using advance analytical techniques such as UV-Visible spectroscopy, scanning electron microscopy (SEM), and Fourier transform infra-red (FTIR) spectroscopy. The electrical conductivity of the samples was obtained using a four-in-line DC electrical conductivity meter. All the samples were found to exhibit the characteristic peaks of polypyrrole in their UV-visible and FTIR spectra. The electrical conductivity study reveals their electrically semi-conducting nature.

Key words: Polypyrrole, DC electrical conductivity, *In situ* polymerization, Scanning electron microscopy, Fourier transform infrared spectroscopy.

1. INTRODUCTION

Polymers are natural or manmade materials which are made small units joined together in a repetitive manner. The repeating unit is termed as "mer" or a basic unit; therefore, "polymer" meaning many repeating units. These monomers are typically made of carbon and hydrogen and sometimes contain chlorine, fluorine, nitrogen, oxygen, phosphorous, sulfur, silicon, etc., in their basic structure. At present, the polymers (natural and synthetic) play a key role our daily life due to their special properties such as a wide range of stiffness, strength, heat resistance, and low density [1,2].

Since the early days, polymers were considered as electrical insulators and so were their early applications as well. However, this idea was challenged with the remarkable discovery of electrically conducting polymers during the late 1970s by Shirakawa *et al*. [3]. These electrically conducting were also called as "synthetic metals." Among the many members of the conducting polymers, polypyrrole has attracted special attention due to its easy synthesis, reversible redox chemistry, stability, economical preparation, etc. [3-6].

The conducting polymers are perceived as macromolecules having the fully conjugated sequence of bond along the backbone which acquires a positive or negative charge by oxidation or reduction process. The conducting polymers have extended conjugated π electron system and are highly susceptible to chemical or electrochemical oxidation or reduction [7,8]. Therefore, the electrical and optical properties of conducting polymers could be precisely altered by carefully controlling the process of oxidation and reduction. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision switching from a highly conducting state through semiconducting to an insulating state [9-15]. The electrical conductivity of conducting polymers depends on methods of preparation, methods of processing, degree of crystallinity as well as temperature [4-8]. The structure of some most common conducting polymers is shown in Figure 1.

Among the large variety of conducting polymers, polypyrrole is an attractive material because of its relatively easy synthesis. It can be obtained as fine powder using the oxidative polymerization of monomer by selected transition metal ion in water or various other solvents. The reaction of polypyrrole with ferric chloride is very fast and the product is formed in the form of black powder [5,7]. Polypyrrole exhibits interesting properties and high electrical conductivity, easy to prepare, good environmental stability, electrocatalytic activity, etc. [5,7,16,17]. Therefore, it has been widely used in electrochemical applications such as electrode material in electrochemical energy storage [18], as catalytic support in fuel cell [19], in supercapacitors [20], and bio-sensing [21].

2. EXPERIMENTAL

2.1. Materials

Pyrrole (Merck, India), potassium persulfate ($K_2S_2O_8$, CDH India), $FeCl_3$ (CDH, India), potassium dichromate ($K_2Cr_2O_7$, CDH, India), Hexane (Merck, India), dimethyl sulfoxide (DMSO, Merck India), ethanol (Merck, India), and distilled water. All chemicals were used as received.

***Corresponding author:**
Email: shahidzahir@gmail.com

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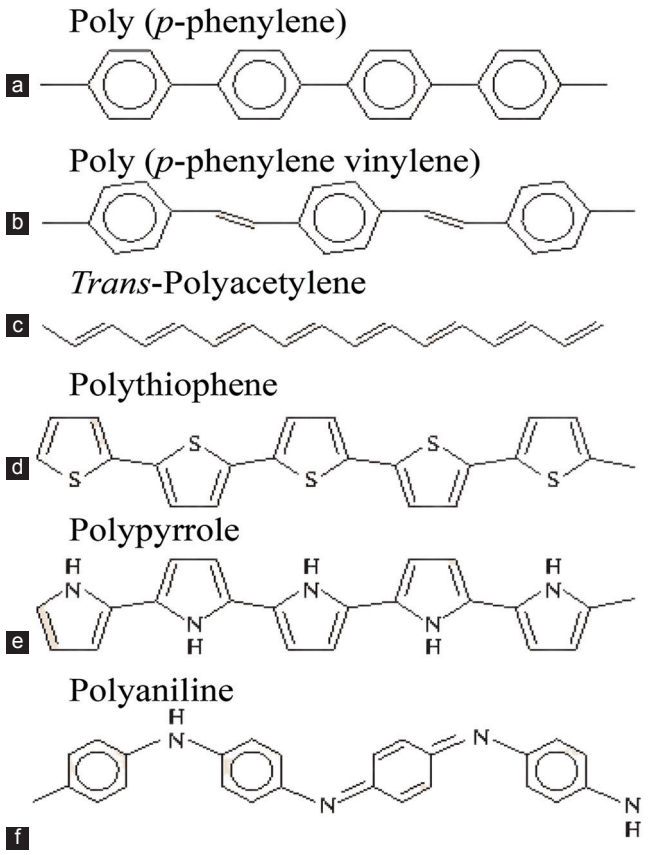

Figure 1: (a-f) The structure of some most common conducting polymers.

2.2. Synthesis of Polypyrrole

The polypyrrole was synthesized by chemical oxidative polymerization of pyrrole [5,7,22]. Hundred milliliters of double-distilled water was taken in 200 ml beaker. A calculated amount of oxidant was dissolved in it. When the oxidant was fully dissolved 1 ml (14.4 mmol), pyrrole in above oxidant solution was added and it was stirred for 6 h at room temperature. After completion of the polymerization reaction, the dark black precipitate was obtained, it was filtered, washed repeatedly with ethanol and distilled water until the filtrate was colorless. Thus, the obtained product was dried in an air oven at 60° temperature for 6 h. The details of synthesis parameters are given in Table 1. Polymerization steps of pyrrole into polypyrrole are shown in Figure 2.

2.3. Characterization

The prepared samples were characterized by advance analytical techniques, such as Fourier transform infrared (FTIR) spectra, UV-visible spectra, and scanning electron microscopy (SEM) micrographs were obtained using Perkin-Elmer 1725 instrument on KBr pellets, Shimadzu UV-Vis spectrophotometer (model 1601), and JEOL-JSM 6510-LV (Japan), respectively. Electrical conductivity was measured using a four-in-line DC electrical conductivity meter equipped with a temperature controller (PID-200, Scientific Equipment's, Roorkee, India)

3. RESULTS AND DISCUSSION

3.1. FTIR Spectroscopy Studies

The FTIR spectra of all the sample, namely, SA-1, SA-2, SA-3, SA-4, SA-5, and SA-6 are shown in Figure 3. In case of SA-1, the peaks observed at about 3421 cm^{-1}, 2918 cm^{-1}, 1563 cm^{-1}, 1459 cm^{-1}, 1321 cm^{-1}, 1177 cm^{-1}, and 1041 cm^{-1} may be ascribed to the stretching vibrations of N-H, C-H, C=C, C-C, C=N, C-N, and =C-H bonds present in polypyrrole chain, respectively [5,7,23]. The peak appeared at around 926 cm^{-1} is attributed to the $C=N^{+}$-C stretching vibrations, which confirmed the formation of polarons, that is, charge carriers [7,22,23]. All the other samples showed similar peaks like SA-1 with a slight shift in the characteristic peaks of polypyrrole indicating the successful synthesis of polypyrrole. The characteristic peaks related to polypyrrole chain and their corresponding bond vibrations are given in Table 2.

Table 1: Details of synthesis parameters used during polymerization of pyrrole.

Sample code	Oxidants	Medium	Pyrrole:oxidant ratio
SA-1	$K_2S_2O_8$	Water	1:1
SA-1_1			1:2
SA-1_2			2:1
SA-2	$FeCl_3$	Water	1:1
SA-2_1			1:2
SA-2_2			2:1
SA-3	$K_2Cr_2O_7$	Water	1:1
SA-3_1			1:2
SA-3_3			2:1
SA-4	$K_2S_2O_8$	DMSO	1:1
SA-5	$K_2S_2O_8$	Hexane	1:1
SA-6	$K_2S_2O_8$	Ethanol	1:1

3.2. UV-visible Spectroscopic Studies

To evaluate the optical properties, we have recorded the UV-visible spectra of all the samples, namely, SA-1, SA-2, SA-3, SA-4, SA-5, and SA-6, as shown in Figure 4. The band detected at around 362 nm, 358 nm, 345 nm, 501 nm, 490 nm, and 491 nm for SA-1, SA-2, SA-3, SA-4, SA-5, and SA-6, respectively, revealed the π-π* electronic transition of benzenoid rings [24]. In case of SA-1 and SA-2, the peaks were more prominent due to efficient π-π^{*} electronic transition which may be related to the greater electrical conductivity of these two samples as compared to other four sample (i.e., SA-3, SA-4, SA-5, and SA-6).

3.3. SEM Studies

The SEM micrographs of SA-1, SA-2, SA-3, SA-4, SA-5, and SA-6 are shown in Figure 5. The surface of the SA-1 consists of globular particles. The SA-2 and SA-6 also consist of globular particles like SA-1, but the size of particles is different in all three cases. SA-3 consists of spherical particles agglomerated with each other. The morphology of SA-5 is completely different from other samples. It consists of a sheet-like structure with some round particles. Thus, it may be concluded that the morphology of polypyrrole changes with changing oxidant as well as the solvent system.

3.4. DC Electrical Conductivity Studies

DC electrical conductivity of all the synthesized samples (i.e., SA-1, SA-2, SA-3, SA-4, SA-5, and SA-6) was evaluated by a four-in-line probe with a temperature controller PID-200 (Scientific Equipment, Roorkee, India). The following equation was applied for calculating DC electrical conductivity (σ):

$$\sigma = [\ln 2\ (2S/W)]/[2\pi S\ (V/I)] \quad (1)$$

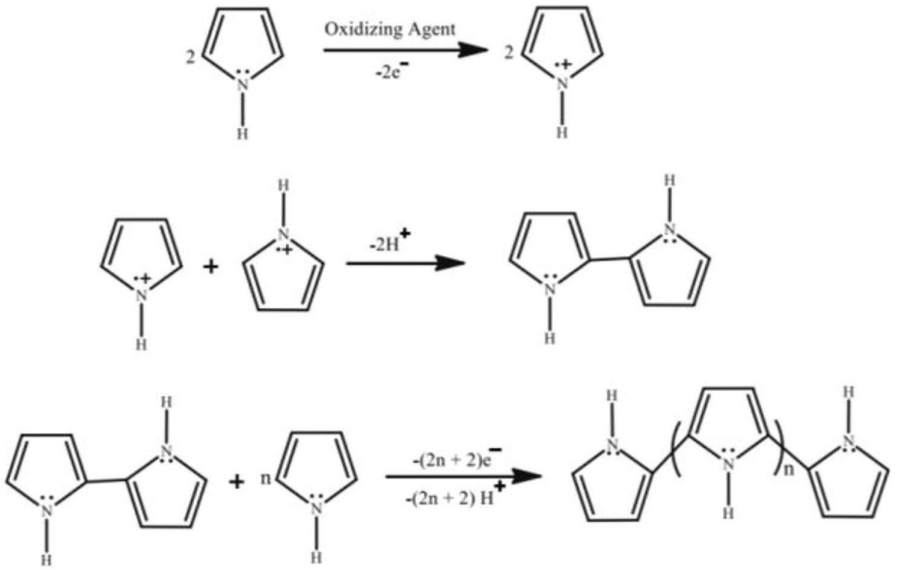

Figure 2: Representative steps of polymerization of pyrrole.

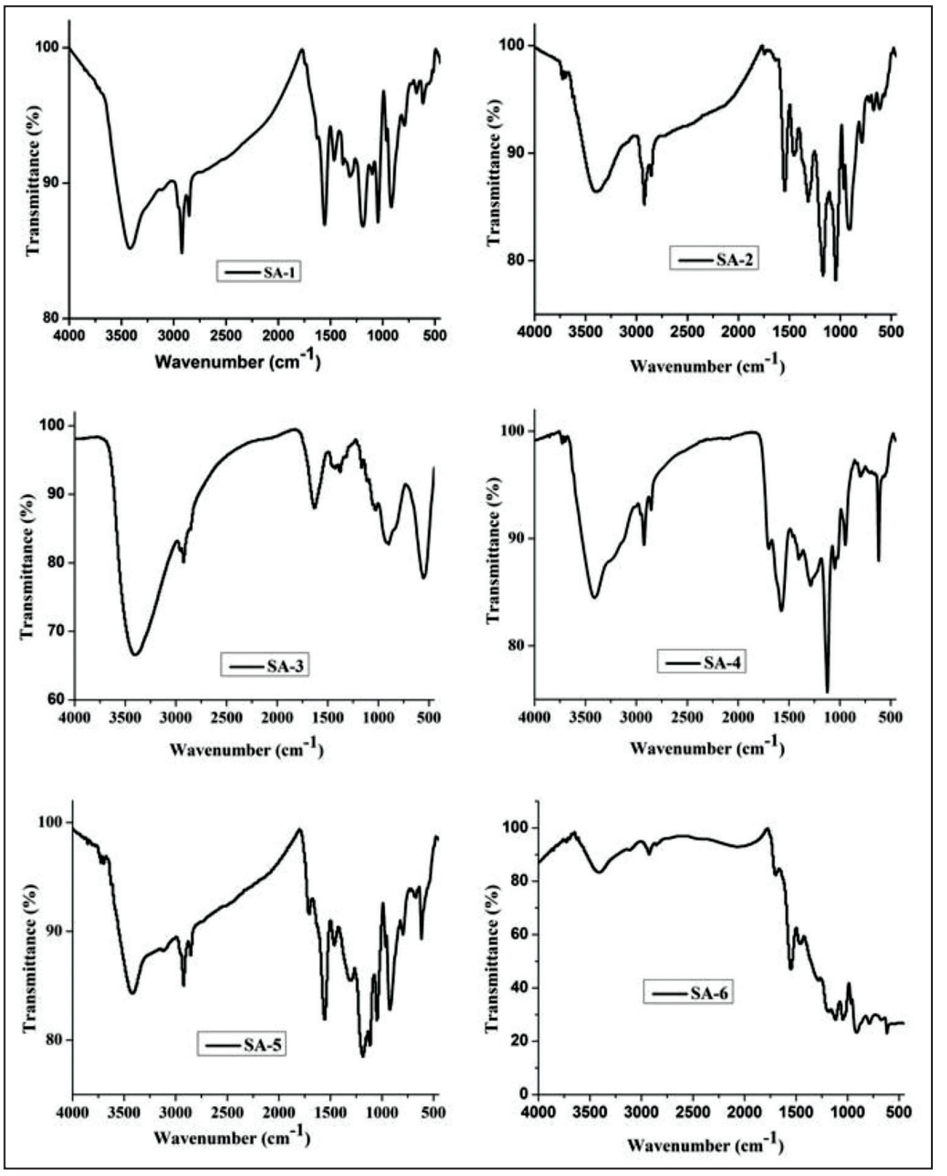

Figure 3: FTIR spectra of all the as-synthesized samples.

Table 2: Details of peaks obtained in FTIR spectra of synthesized samples.

S. No.	Sample code	N-H (cm^{-1})	C-H (cm^{-1})	C=C (cm^{-1})	C-C (cm^{-1})	C=N (cm^{-1})	C-N (cm^{-1})	=C-H (cm^{-1})	$C=N^{+}$-C (cm^{-1})
1.	SA-1	3421	2918	1563	1459	1321	1177	1041	926
2.	SA-2	3400	2920	1550	1460	1320	1180	1040	918
3.	SA-3	3410	2921	1571	1440	1340	1170	1040	905
4.	SA-4	3401	2926	1573	1415	1315	1150	1049	940
5.	SA-5	3430	2922	1560	1460	1310	1179	1050	929
6.	SA-6	3420	2930	1559	1463	1302	1172	1042	911

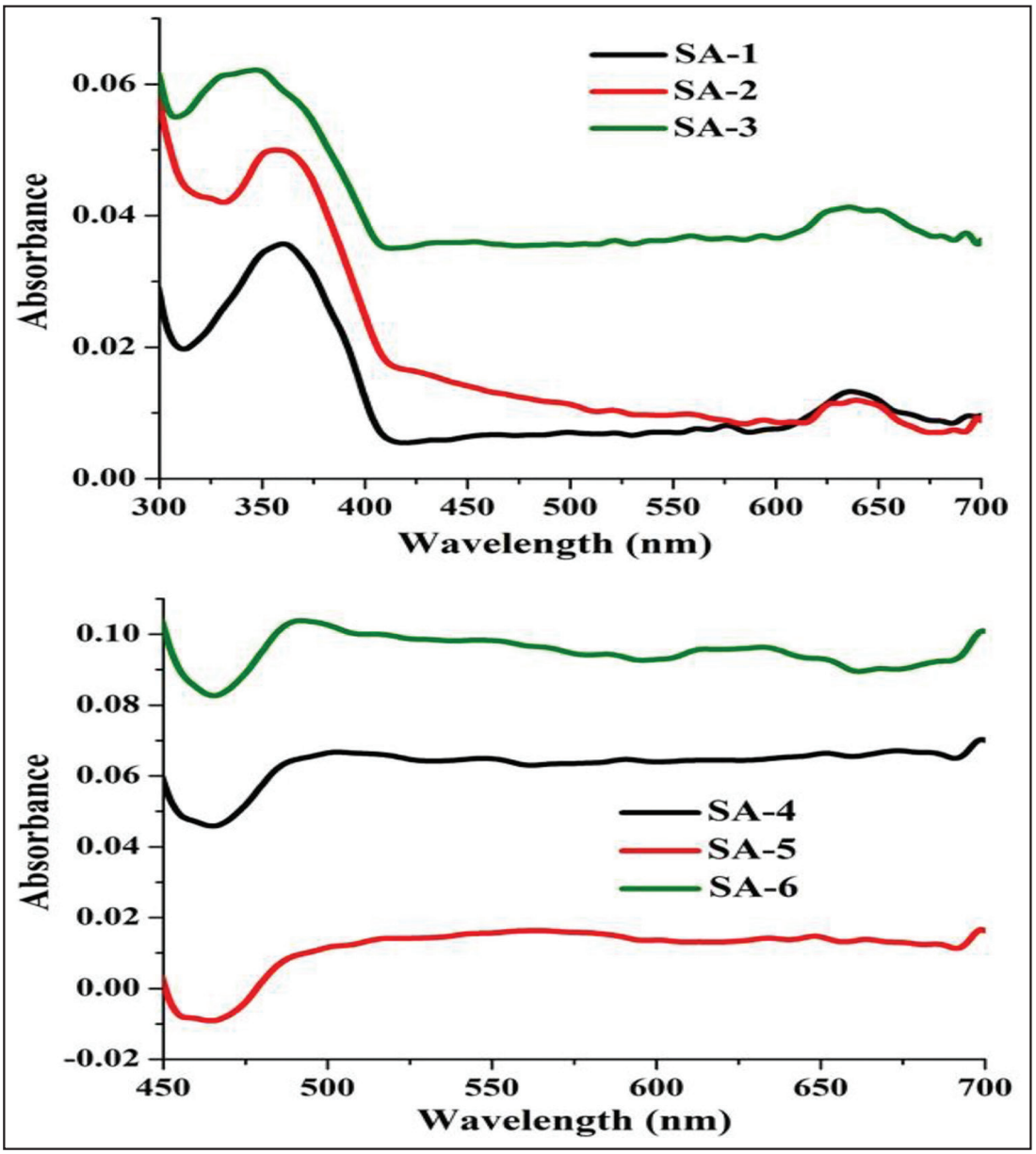

Figure 4: UV-visible spectra of all the as-synthesized samples.

Where: I, V, W, and S represent the current (A), voltage (V), pellet-thickness (cm), and probe-spacing (cm), respectively [11,24].

The electrical conductivity was found to be 7.579×10^{-3} Scm^{-1}, 3.721×10^{-4} Scm^{-1}, 1.041×10^{-6} Scm^{-1}, 4.678×10^{-5} Scm^{-1}, 1.854×10^{-6} Scm^{-1}, and 5.238×10^{-5} Scm^{-1} for SA-1, SA-2, SA-3, SA-4, SA-5, and SA-6, respectively (Figure 6).

These results showed that among all the oxidants and solvent used in this analysis, $K_2S_2O_8$ acted as the best oxidant in an aqueous medium. The electrical conductivity obtained in case of $FeCl_3$ as an oxidant in aqueous medium was comparatively high as compared to other four samples, that is, SA-3, SA-4, SA-5, and SA-6. The greater conductivity in case of SA-1 and SA-2 may occur due to generation of a greater number of polarons (charge carriers) of

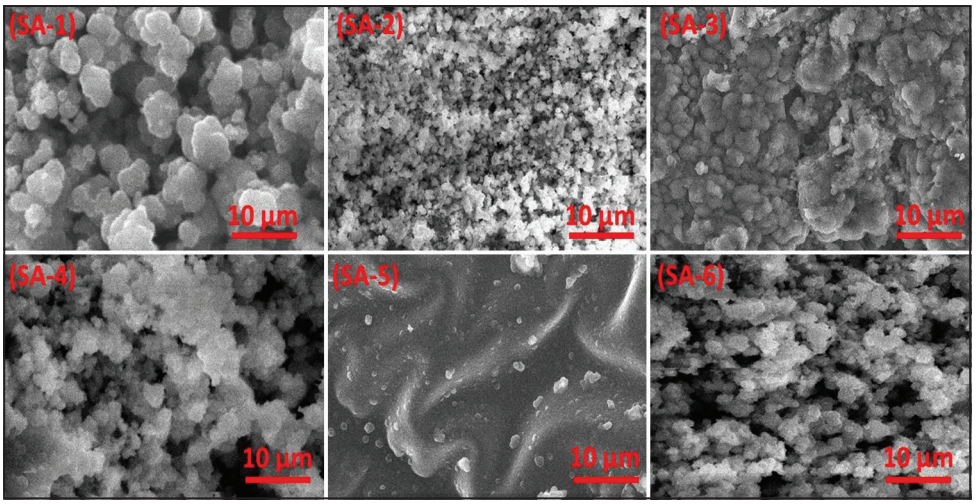

Figure 5: SEM images of all the as-synthesized samples.

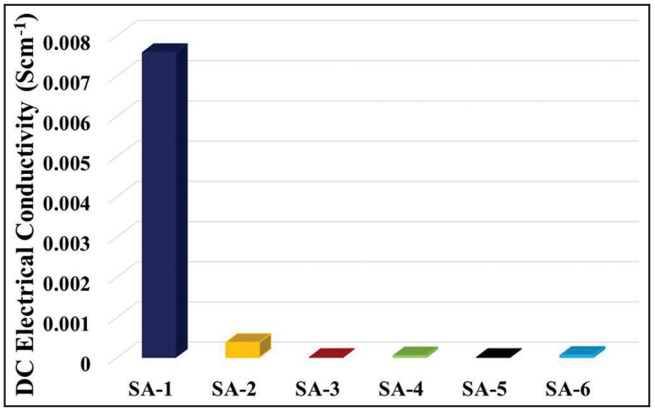

Figure 6: DC electrical conductivity of the as-synthesized samples.

polypyrrole by comparatively strong oxidizing properties of $K_2S_2O_8$ and $FeCl_3$.

4. CONCLUSIONS

In this study, we have synthesized polypyrrole by simple and cost-effective *in situ* chemical oxidative polymerization method using different oxidant (potassium persulfate, anhydrous ferric chloride, and potassium dichromate) as well as different solvent system (double distilled water, DMSO, hexane, and ethanol). The successful formation of polypyrrole was confirmed by characteristic peaks observed in the FTIR spectra of each sample. The morphology of the materials was determined by SEM. The optical properties of all the samples were investigated by UV-visible spectroscopy. Finally, DC electrical conductivity of all the samples was calculated by the four-in-line probe technique at room temperature. The sample prepared using potassium persulfate as an oxidant and double distilled water as a solvent showed the highest electrical conductivity (7.579×10^{-3} Scm^{-1}). However, the conductivity of sample prepared in aqueous medium using anhydrous ferric chloride as an oxidant also exhibited fairly good electrical conductivity (3.721×10^{-4} Scm^{-1}). Thus, polypyrrole synthesized in aqueous medium using potassium persulfate or anhydrous ferric chloride can be utilized as good semiconducting material in various electrical/electronic applications.

5. ACKNOWLEDGMENT

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6. CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

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