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(Research Article)

# Synthesis and characterization of polypyrrole thin films

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## Abstract

The present study emphasizes on growth of Polypyrrole thin films by modified chemical bath deposition method on glass substrate at room temperature. These as deposited thin films are characterized for optoelectronic, physicochemical properties. The structural analysis carried from Fourier transform infrared radiation (FTIR) represents deep at 810.10 $\text{cm}^{-1}$, 887.26 $\text{cm}^{-1}$ attributed to C–H Bond while 1041.56, 1712.79 $\text{cm}^{-1}$ infers to C-H bond N–C stretch bending, while the characteristic peaks at 1519.91 $\text{cm}^{-1}$ and 1550.77 $\text{cm}^{-1}$ correspond to the C=C stretching. The X-ray diffraction (XRD) pattern obtained shows amorphous nature of the Polypyrrole with presence of peak corresponding to glass substrate. Surface morphology as observed from the scanning electron microscope (SEM) shows granular structured grain distribution over the substrate surface with higher porosity having interlinked granules. Peaks at 328 and 420nm in UV Vis absorbance spectrum revealed bond to bond transition with exciton induced charge transfer, the energy band gap calculated from the extra plotting of UV-Vis data is 2.8eV which corresponds for exciton induced charge transformation. The electrical characteristics confirms ohmic behavior of the samples confirming grain induced charge mobility and transportations.

**Keywords:** Polypyrrole; Chemical polymerization; Thin films; Granular surface; Electrical conductivity; Optical band gap

## 1. Introduction

Environmental challenges in the present era are at its peak for human health and other living organisms too, which has given rise in urgent attention for development of sensors which could detect and react for minute changes in the proportion of hazardous gases causing challenges to living beings. There are several organic and inorganic materials available in and around which are regularly used for development of gas sensors in particular. These materials find various opportunity for development of physical and chemical interaction-based sensors [1-3]. Amongst them polymer materials being conjugated double bond Hydrocarbon compound with nitrogen element which has attracted much attention of the researchers for development of different electronic gadgets, out of it, polyaniline, polypyrrole are some of the polymers which are universally considered for physical and chemical sensors developments [4-5]. Literature survey has revealed that there are numerous physical methodologies available for synthesis of hydrocarbon polymer but very few reports are there mentioning about use of chemical route for polypyrrole thin film synthesis [6-8]. Even the thin films developed using the chemical route have advances over other methods like stability of the material, stoichiometry and composition. Hence considering this as one of the scope along with other advances like ease of synthesis, large area deposition and synthesis controlled optoelectronic and physicochemical properties we have tried to synthesize the polypyrrole thin film using modified chemical route over the glass substrate at room temperature [9-11]. Surface morphology of room temperature synthesized thin films are very particular, granular and defect free which provide an opportunity for chemisorption and physisorption sensing phenomenon, thereby enhancing the chances of polypyrrole becoming good material for sensor development.

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These as deposited polypyrrole thin films are characterized for physicochemical and optoelectronic properties using Fourier transform infrared spectroscopy (FTIR) for ionic chemical bonding and composition identification, X-ray diffraction pattern (XRD) for structural confirmation while scanning electronic microscopy images used for surface morphology studying, the UV-Vis study conducted for electronic transitions and energy band gap calculations while I-V study is used for resistivity and conductivity property analysis.

## 2. Experimental

The chemical oxidative polymerization of pyrrole is one of the first but still the most popular method for preparation of Polypyrrole as it is a simple and fast process with no need for special equipment. In the chemical polymerization process, pyrrole is oxidized by chemical oxidizing agents, using ammonium per-sulphate [12, 13]. These oxidants are able to oxidize the pyrrole at the initial stages and began polymerization [14, 15].

According to this mechanism, in the initiation step, the oxidation of a pyrrole monomer takes place resulting in chemically active radical cations of the monomer, coupling of two in the initiation step generated radical cations and then de-protonation produces chain of C-H bonds. In propagation steps, the bi-pyrrole is oxidized again and coupled with another oxidized segments. Re-oxidation, coupling, and de-protonation continue to form soluble oligomers and finally insoluble black polymer pyrrole deposited over the substrate surface [16].

Monomer as Pyrrole purchased from Sigma-Aldrich (C4H5N, M.W. 67.09) reagent grade. Analytical grade ammonium per-sulphate (APS) was used as oxidizing agent. The cleaning of the substrate is an important factor in thin film deposition, since the nucleation and subsequent growth of the film mainly depends upon substrate surface. Hence prior to deposition, glass substrates washed to free off the emery particles, ultrasonically treated in double distilled water for 40 minutes and finally air dried [17]. The AR grade pyrrole, $H_2SO_4$ and ammonium persulphate (APS) were used for the deposition of Polypyrrole thin films. Initially, separate solutions of 0.1 M of $H_2SO_4$, 0.1 M APS and 0.1 M pyrrole were prepared in double distilled water (DDW). Here, APS acts as an oxidizing agent to oxidize pyrrole. Briefly, $H_2SO_4$ and APS (each 25 ml) solutions were mixed together and stirred for 20 minutes [1-5]. Subsequently, well-cleaned glass substrates were dipped vertically in this solution and pyrrole solution was added drop-wise in the bath till solution became black. After 40 min, well-uniform and black colored Polypyrrole thin films were deposited on glass substrate (Figure 1). The substrates were taken out from bath and washed in DDW to remove the residue of reactants [18, 19].

These as deposited thin films are characterized for optoelectronic and physicochemical properties, the X ray diffraction pattern (XRD) carried on D8 Bruker model Venture. The elemental composition and ionic bonds confirmed from the data observed over Fourier transform infrared (FTIR) recorded over Shimadzu IR Affinity 1S, while scanning electron microscopy (SEM) images observed on JEOL JSM model 6360, Optical absorbance spectrum measured over the range of 200 to 1000nm over Perkin Elmer λ.

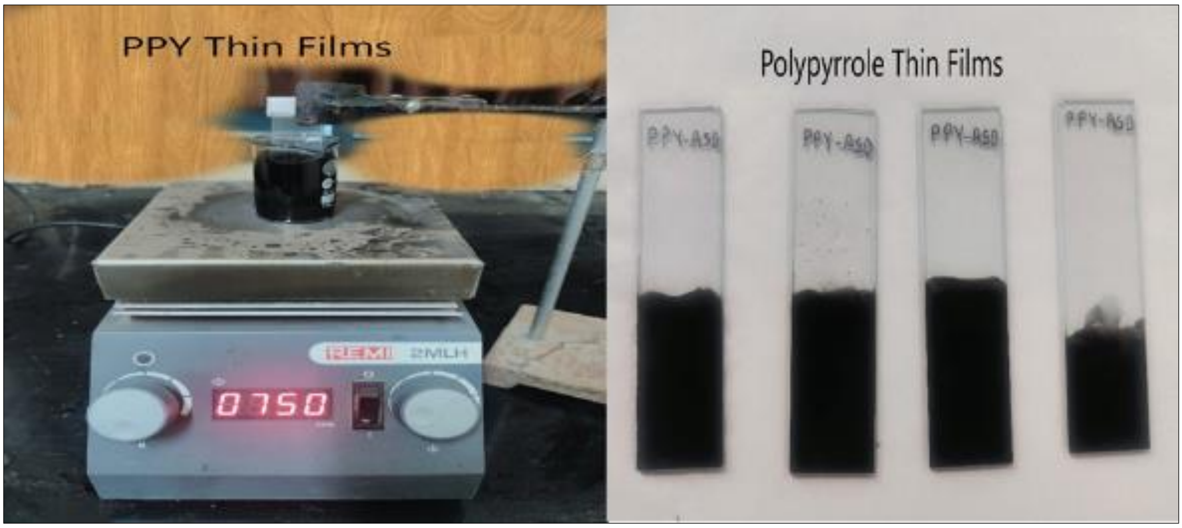

**Figure 1** Schematic of Polypyrrole synthesis along with image of synthesized thin films

## 3. Results and Discussion

### 3.1. FTIR Spectroscopy Analysis

The characteristic stretching bonds of the materials with wavenumber are summarized. However, these spectra reveal the same peaks for sample and no extra peaks due to employment of various oxidants entails the purity of materials. The FTIR spectra of POLYPYRROLE represented in Figure 2. The most prominent and broad absorption peak at 810.10 cm$^{-1}$, 887.26 cm$^{-1}$are attributed to C–H Bond out of plane vibration. The characteristic peaks at 1041.56 are attributed to C-H bond in plane vibration. The peaks at 1712.79 cm$^{-1}$ are attributed to N–C stretch bending [20-21]. The characteristic peaks at 1519.91 cm$^{-1}$ and 1550.77 cm$^{-1}$ correspond to the C=C stretching. The occurrence of small peaks at 3456.44 cm−1 is assigned to presence of N–H stretching vibrations. The peaks at 1195.87 cm$^{-1}$are attributed to N-H Bonding in the molecule. The peaks observed in the present work match well with the ones available in the literature confirming the formation of Polypyrrole. In addition, the amorphous nature of polypyrrole [22].

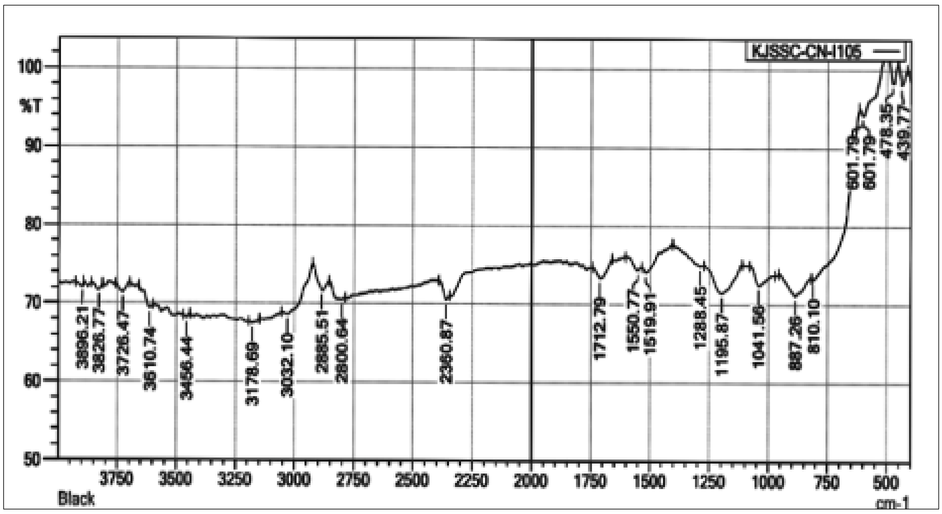

**Figure 2** FTIR spectrum of the Polypyrrole thin films

### 3.2. X-Ray Diffraction Analysis

The X-Ray diffraction pattern of Polypyrrole thin films obtained is shown in Fig. 3, absence of diffraction peak in the entire pattern indicates amorphous nature of Polypyrrole while broad peak observed at 2θ=23.96° corresponds for the glass substrate [22-23]. Polypyrrole being polymeric material with C-H and C-N binding it possesses the amorphous nature.

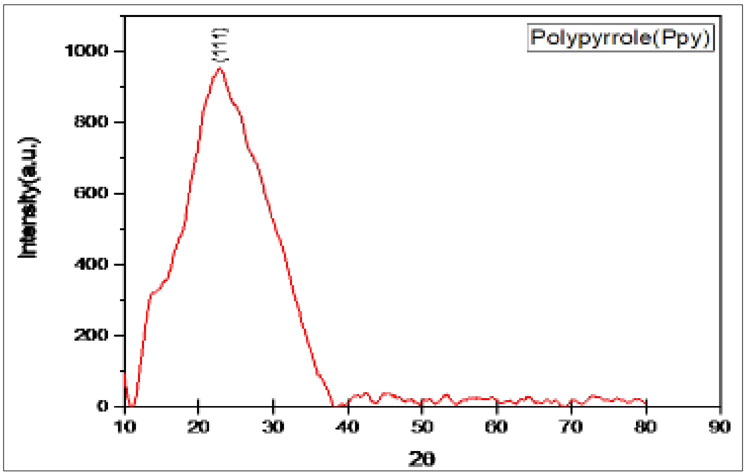

**Figure 3** The X-Ray diffraction pattern of Polypyrrole thin films

### 3.3. Scanning Electron Microscopy (SEM) Analysis

The two-dimensional surface morphology of the Polypyrrole thin films has been studied using SEM images. Fig. 4 (a), (b) and (c) shows the SEM images of Polypyrrole thin film at different magnifications. Formation of 3D architecture of Polypyrrole surface with coalesced nano particles can be clearly seen from SEM images. The low magnification (Fig. 4 (c)) image confirms the formation of spherical granular bunches of interconnected with each other with sufficient porous nature, images revealed compact, crack free, smooth, randomly distributed and uniform morphological coverage of Polypyrrole on substrate surface, micrographs shows the agglomeration of interconnected nanograins. Literature revealed that morphology of Polypyrrole films strongly depends upon nature of anionic oxidizing agents and preparation methods [24-25]. High magnified image (Fig. 4 (a), (b)) gives a description that these grains are approximately of average size in the range 20-50 nm. The contrast in the SEM image (Fig. 4 (c)) shows that the film has hollow cavities which are highly porous. The porous nature of the Polypyrrole makes it a potential candidate for various surface related applications [26].

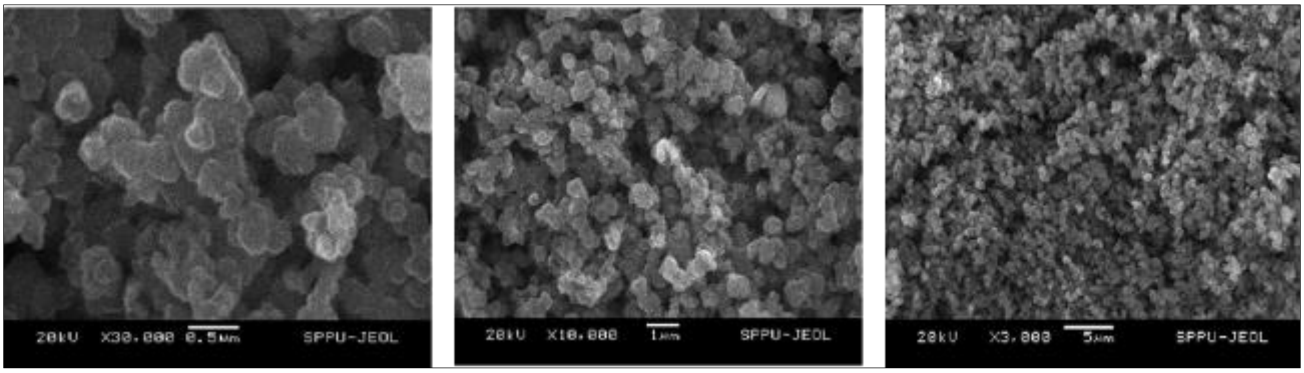

**Figure 4** (a), (b) and (c) SEM images of Polypyrrole thin films with different magnifications

### 3.4. UV-Vis Spectroscopy analysis

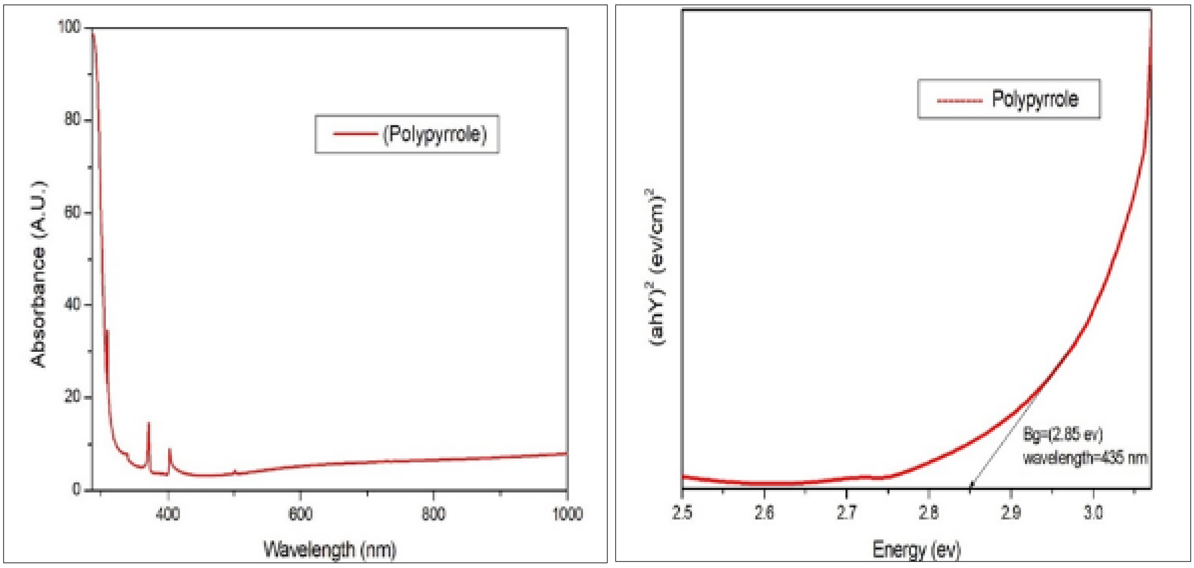

**Figure 5** UV-Vis absorbance spectrum of the Polypyrrole thin films along with plot for energy band gap calculations

The optical absorbance spectra drawn as a function of wavelength against absorbance, as represented in Fig. 5, peak at 420 and 860 nm corresponds for intra-band and exciton induced band transitions respectively, while the energy band gap of calculated using the absorbance spectrum obtained to be 2.85eV corresponds to grain growth and grain boundry charge transportations through surface plasmon and ionic transportations for electrical charge motions [25-27].

### 3.5. Electrical study

Figure 6 shows variation of electrical resistance as a function of temperature obtained from polypyrrole thin films. In this case it was observed that as temperature increases the electrical resistance decreases and hence conductivity increases. This suggests that the thermally activated behavior of conductivity has been confirmed. The decrease in resistance may be due to increase of efficiency of charge transfer in polypyrrole with increase in temperature [28-29]. The thermal curling affects the chain alignment of the polymer, which leads to increase of conjugation length and which in turn brings about the decrease in resistance. Also, there will be molecular rearrangement on heating, which make the molecules favorable for electron delocalization.

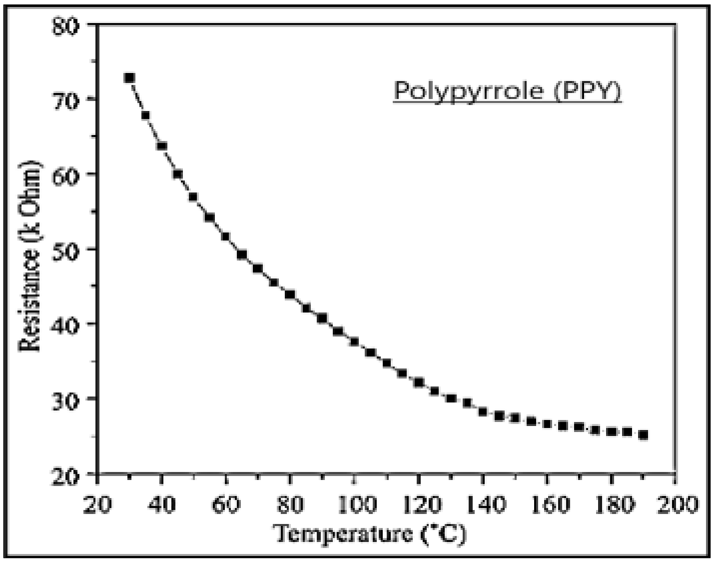

**Figure 6** Electrical Resistance Vs Temperature obtained from the Polypyrrole thin films

## 4. Conclusion

From the above study it can be concluded that the polypyrrole thin films can be grown using simple, cost-effective, modified chemical bath deposition over glass substrate at room temperature. From FTIR spectrum elemental ionic bonding along with the compositions at810.10 cm$^{-1}$, 887.26 cm$^{-1}$ attributed to C–H bond while 1041.56, 1712.79 cm$^{-1}$ infers to C-H bond N–C stretch bending, the characteristic peaks at 1519.91 cm$^{-1}$ and 1550.77 cm$^{-1}$ correspond to the C=C stretching finalizes the polypyrrole formation. XRD confirms amorphous nature of the thin films with observation of separate peak for glass substrate. SEM shows porous nature of the film with granular distribution over the substrate surface, the UV Vis absorbance confirms polaron based electronic charge transfer along with band-to-band transitions. I-V graph represented the semiconducting nature of materials with proportionate current voltage response confirming the grain growth and electronic charge diffusion over the surface.

## Compliance with ethical standards

### *Disclosure of conflict of interest*

No conflict of interest to be disclosed.

## References

[1] M.A. Chougule, S.G. Pawar, P.R. Godse, R.N. Mulik, S.Sen, V.B. Patil, Scientific Research, Soft Nanoscience Letters, 1 (2011) 6-10.

[2] S.S. Shinde, G.S. Gund, D.P. Dubal, S.B. Jambure, C.D. Lokhande, Electrochimica Acta 119 (2014) 1-10.

[3] A.K. Minkstimiene, V. Mazeiko, A. Ramanaviciene, A. Ramanavicius, Colloids and Surfaces A: Physicochemical and Engineering Aspects 0927-7757 (2015) 00418-5.

[4] A.L. Pang, A. Arsad, M. Ahmadipour, Polymers Advanced Technologies, 32 (2021) 1428–1454.

[5] U. Sree, Y. Yamamoto, B. Deore, H. Shigi, T. Nagaoka, Synthetic Metals 131 (2002) 161–165.

[6] H.S. Abdulla, A.I. Abbo, International Journal of Electrochemical Science, 7 (2012) 10666 –10678.

[7] S.S. Shinde, G.S. Gund, V.S. Kumbhar, B.H. Patil, C.D. Lokhande, European Polymer Journal S0014-3057 (2013) 00389-3.

[8] S.Sakthivel, A. Boopathi, Journal of Chemistry and Chemical Science, 4 (2014) 150-155.

[9] D.P. Dubal, S.V. Patil, A.D. Jagadale, C.D. Lokhande, Journal of Alloys and Compounds, 509 (2011) 8183-8188.

[10] T.A. Skotheim, Handbook of Conducting Polymers, Marcel Dekker, New York, 1986.

[11] T.A. Skotheim, R. Elsenbaumer and J. Reynolds, Hand-Book of Conducting Polymers," Marcel Dekker, New York, 1998.

[12] G.G. Wallace, G. Spinks and P.R. Teasdale, Conductive Electroactive Polymers Technomic, New York, 1997.

[13] K.L. Chopra, Thin Film Phenomena, McGraw Hill Book Co, New York, 1969.

[14] S.P. Palaniappan, P. Manisankar, Mater. Chem. Phys. 122 (2010) 15.

[15] C. Yang, T. Wang, P. Liu, H. Shi, D. Xue, Solid State Mater. Sci. 13 (2009) 112.

[16] H.J. Kharat, K.P. Kakade, P.A. Savale, K. Dutta, P. Ghosh and M.D. Shirsat, Polymers for Advanced Technologies, 18 (2007) 397- 402.

[17] B. Tian, G. Zerbi, Journal of Chemical Physics, 92 (2009) 3886-3891.

[18] K. Arora, A. Chaubey, R. Singhal, R.P. Singh, M.K. Pandey, S.B. Samanta., B.D. Malhotra, Bio- sensors and Bioelectronics, 21 (2006) 1777- 1783.

[19] K. Leonavicius, A. Ramanaviciene, A. Ramanavicius, Langmuir 27 (2011) 10970–10976.

[20] M. Taunk, A. Kapil, S. Chand, J. Mater. Sci. Mater. Electron. 22 (2011) 136–142.

[21] J.A. Pomposo, E. Ochoteco, C. Pozo, P.M. Carrasco, H.J. Grande, F.J. Rodriguez Polym. Adv. Technol. 17 (2006) 26–29.

[22] M.M. Castillo-Ortega, M.B. Inoue, M. Inoue, Synthetic Met. 28 (1989) 65–70.

[23] R. Stankovic, V. Laninovic, S. Stankovic, S. Jovanovic, M. Vojnovic, Macromol. Chem. Phys. 196 (1995) 825–832.

[24] V. Bocchi, L. Chierici, G.P. Gardini, R. Mondelli, Tetrahedron 26 (1970) 4073–4032.

[25] Z. L. Wang, X. Y. Kong, Y. Ding, P. Gao, W. L. Hughes, R. Yang and Y. Zhang, Advanced Functional Materials, 14 (2004) 943-956.

[26] H. Shiigi, M. Kishimoto, H. Yakabe, B. Deore and T. Nagaoka, Analytical Sciences, 18 (2002) 41-44.

[27] M. Leclerc, G. D'Aparno and G. Zotti, Synthetic Metals, 55 (1993) 1527-1532.

[28] F. Zuo, M. Angelopoulos, A. G. MacDiarmid and A. J. Epstein, Physical Review B: Condensed Matter and Materials Physics, 36 (1987) 3475-3478.

[29] A. Kobayashi, H. Ishikawa, K. Amano, M. Satoh and E. Hasegawa, Journal of Applied Physics, 74 (1993) 296-299.