

CHARACTERIZATION AND SYNTHESIS OF 3-PSA AND 4-SBA POTASSIUM SALT DOPED POLYPYRROLE

P.G. Rajas^a, N. S. Ghotkar^b, V. M. Raut^c,

^aDepartment of Chemistry, Government Vidarbha Institute of Science & Humanities, Amravati.M.S.India.

^bDr. Sau. Kamaltai Gawai Institute of ENginnering & Technology, Darapur., Amravati M.S. India.

^cGovernment Science College Gadchiroli.M.S. India.

Abstract: Electronically conducting polymers such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy) have become the subject of increased research interest due to a great variety of applications in many fields such as electrochromism, electroluminescence, sensors and energy storage systems etc. Among these conducting polymers special interest has been focused on polypyrrole due to its excellent thermal and environmental stability combined with relatively high level of electrical conductivity.

In the present research work considerable effort have been made to modify the structure of polypyrrole by doping it with 3-pyridine sulfuric acid (PSA) and 4-sufobenzene acid potassium salt (SBA) to study its dynamic electrical and mechanical properties. For this the polymer, polypyrrole was synthesized by chemical oxidation polymerization method. In this synthesis, 1M aqueous solution of pyrrole was mixed with aqueous solution of ammonium peroxydisulphate used as an oxidizing agent. Further modified polypyrrole was synthesized by doping it with 3-pyridine sulfuric acid (PSA) and 4-sufobenzene acid potassium salt (SBA). The reaction was stirred for 4 hours with a magnetic stirrer to get products as a precipitated. The resulting products were vacuum filtered and the precipitate was washed with copious amounts of AR grade distilled water to remove impurities. The polymers, polypyrrole doped with 3-pyridine sulfuric acid(PSA),4-sulfobenzene acid potassium salt (SBA) were dried in desiccators over night and again dried in oven at 40 – 45^o C.

Index Terms - pyrrole, ammonium peroxydisulphate, polypyrrole A.R. grade distilled water etc

1. INTRODUCTION

Polymer are macromolecule developed by the connecting of enormous number of a lot littler atoms. The littler particles that join with one another to frame polymer atom are named monomers and responses by which they consolidate are named polymerization.[1] In nature, unadulterated PPy with benzoid structure is a protector and it should dope with oxidant so as to function as a semiconductor.. Various sorts of anionic dopants, for example, p-toluene sulfonate (PTS),dodecylbenzene sulfonate (DBS), chloride (Cl⁻), sulfate (SO₄⁻), tetrafluoroborate (BF₄⁻) and perchlorate (ClO₄⁻) are basic Molecular size and charge of dopant are the primary factors that impact the conductivity [2]. Among all the directing polymers polypyrrole is the most generally contemplated leading polymer in view of its effectively oxidizable nature, water solvency, business accessibility, high conductivity, best ecological dependability and redox properties.[3] Almost these properties rely on the strategy for planning of polypyrrole just as upon the idea of dopant used.[4] Polypyrrole was the primary polymer indicating high conductivity among all the leading polymers. It was first integrated in 1916 and has a tremendous assortment of utilizations as in biosensors[5], gas sensors[6], coatings[7], wires[8], electrolytic capacitors[11], microactuators[9] and battery electrodes[10] Chemical oxidative polymerization is simple, cheap and fast. It can easily be scaled up. Electrochemically synthesized PPy normally exhibits very poor solubility in all common organic solvents and in water. This limits its processability. To overcome these disadvantages, attempts are made by introducing counter-ions into the polymers backbone. Protonation with an organic acid increases solubility, electronic structure, and crystallinity of PPy [18]. To promote the solubility and processability of PPy, various substituted monomers were proposed to reduce the strong intermolecular interaction between conducting polymer chains in the doped state [19]. But long-chain substituents attached to the monomer ring due to steric interference alters the planarity of the polymer structure. This can be achieved by doping polymer with organic acids such 3-pyridine sulfonic acid and 4-sulfo benene sulfuric acid. The presence of organic sulfonic acid as counter-ion in the polymer strongly affects the conductivity, morphology and thermal stability of bulk PPy [20].Hence the presented study is aimed to synthesis of PPY containing various inorganic and organic dopants,

investigation of yield of product while increasing percentage of dopant and analysis of FTIR spectra and NMR spectra of the prepared polymer. Analysis of yield percentage variation with dopant.

2. EXPERIMENTAL METHODOLOGY

Chemicals:- Pyrrole (98% pure sigma Aldrich) Ammonium per sulphate (APS) as oxidant, 4-sulfobenzene acid potassium salt, 3 pyridine sulfonic acid as a dopant, deionised water as neutral solvent are used for synthesis.

2.1 Preparation of undoped polypyrrole powder. [SPPY]

For synthesis of polypyrrole by chemical bath method, primarily all apparatus were washed with deionised water , rinse in acetone. Pyrrole is used as monomer for preparation of polypyrrole powder. Monomer is prepared by using 1M pyrrole in deionised water. Oxidant solution was prepared 1M concentration of APS in deionised water. The ration of monomer to oxidant was kept 1:2. which means the polymerization proceeds in excess of oxidizing agent. Firstly, Monomer solution was added drop wise in an oxidant solution reaction being carry out at room temperature at 25⁰c . During precipitation heterogeneous reaction occur. Polypyrrole produced was kept unagitated for 24 hours, so that polypyrrole powder settle down at bottom. The polypyrrole powder filter out under vacuum and washed with distilled water several times to remove any impurities present. Polypyrrole dried for 2 days at room temperature.

2.2 Preparaton of doped polypyrrole using following dopant

2.2.1 By using dopant -3- pyridinesulfonic acid.(E₂)

The composites powder were prepared by same procedure mention above only dopant-3-pyridine sulfonic acid with 10%,20%,30%, 40%, 50%,60% w/v added in pyrrole solution before addition of oxidant solution. For example, synthesis A₂,B₂,C₂,D₂,E₂,F₂ in Table 4. Then dopped powder were obtained. After 24hrs it was filtered and washed with distilled water several times to remove any impurities present in it. Doped polypyrrole powder dried for 2 days at room temperature.

2.2.2 By using dopant -4-sulfobenzene acid potassium salt.(E₃)

(a) pyrrole as monomer; (b) ammonium persulfate (APS) as oxidizing agents and (c) 4-sulfobenzene acid potassium salt as doping agents. All of these chemicals were reagent grade (Sigma–Aldrich).

The polymerization was carried out either in neutral solution such as deionised water . An overview of synthesized materials is summarized in Table 3. Typical molar ratio of pyrrole:oxidizing agent:doping agent (when present) was 1:2: dopant 4-sulfobenzene acid with 10%, 20%, 30%, 40%, 50%, 60% w/v, which means the polymerization proceeds in excess of oxidizing agent. For example, synthesis A₃,B₃,C₃,D₃,E₃,F₃ in Table 3 proceeds as follows:

Firstly 1M of pyrrole was added drop wise in dopant at different percent w/v stirred for 4Hrs with magnetic stirrer until pyrrole and dopant agent completely dissolved. and then polymerization take place on drop wise addition above mixture in 1M of oxidant APS and were added to 100 ml of distilled water at 25 °C. This mixture was stirred continuously with the help of magnetic stirred for 4Hr until pyrrole and oxidant dopant mixture completely dissolved. Doped Polypyrrole produced was kept unagitated for 24 hours, so that polypyrrole powder settle down at bottom. The polypyrrole powder filter out under vacuum and washed with distilled water several times to remove any impurities present. Polypyrrole dried for 2 days at room temperature.



3- PSA

4- SBA Potassium salt

Fig:- organic dopant in synthesized ppy: a) 3-pyridine sulphuric acid b) 4- sulphobenzene acid potassium salt

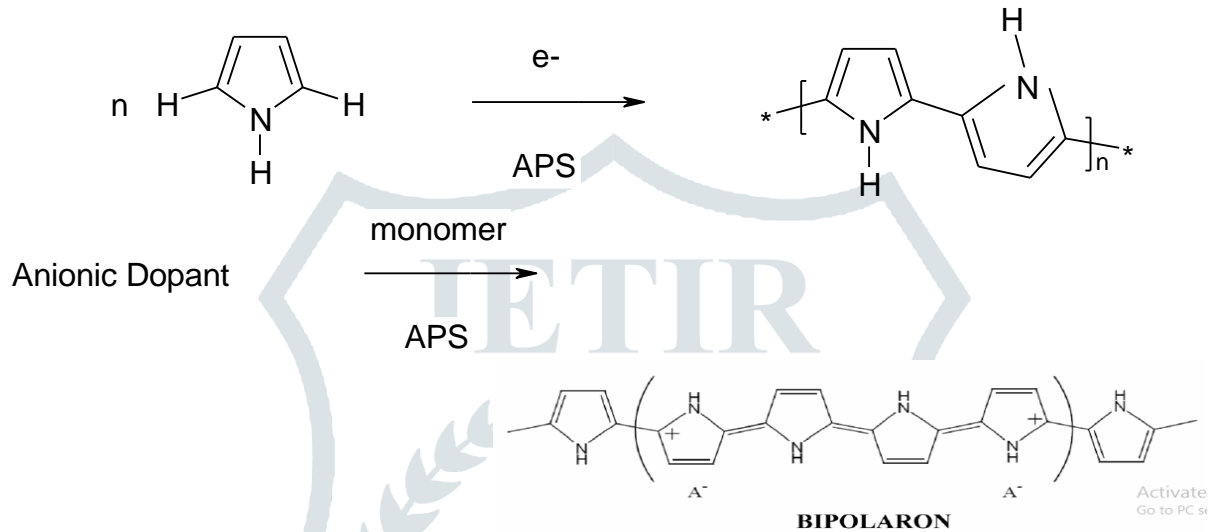


Table1
Overview of synthesized PPY materials. The SO₄²⁻ dopants are residuals of APS .

Synthesis no.	Oxidizing agent	Doping agent	Dopants a waited in product
SPPY	APS	-----	SO ₄ ²⁻
E ₂	APS	3-PSA	Anion 3-PSA, SO ₄ ²⁻
E ₃	APS	K ⁺ (4-SBA)	Anion4-SBA, SO ₄ ²⁻

3. RESULT AND DISSCUSSION

Effect of Yield of Product on concentration of oxidant and dopant

3.1 Preparation of undoped polypyrrole using monomer and oxidant

The yield is given as follows in table.2

Sr.no.	Monomer (1M)	Oxidant (14ml) with different concentration	Yeild in gram	Yield in percentage
1	7ml	0.5M	0.16	2.54
2	7ml	1M	0.22	2.79
3	7ml	1.5M	0.36	3.80
4	7ml	2M	0.51	3.9
5	7ml	2.5M	0.60	4.0

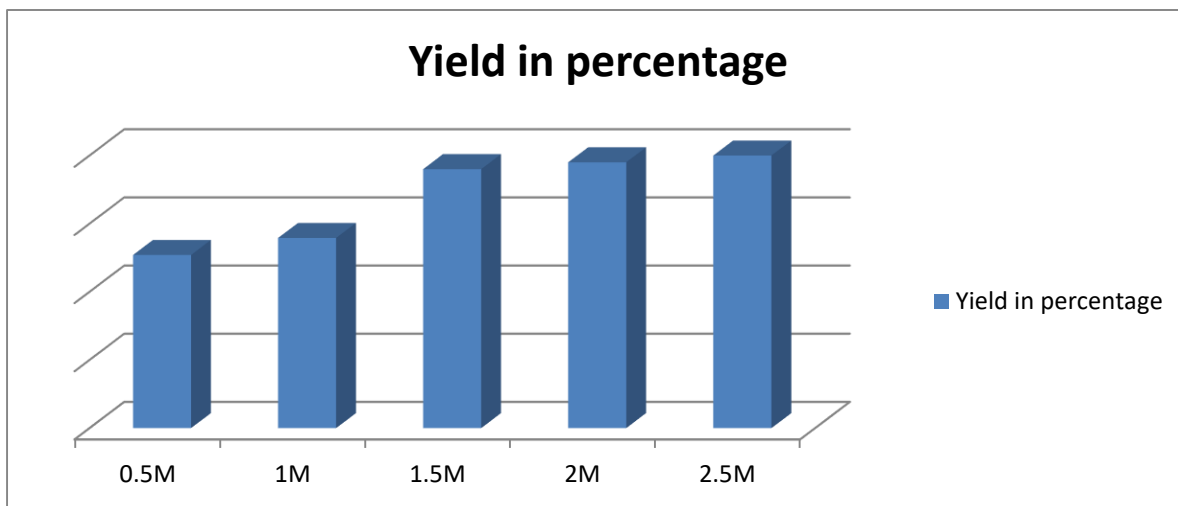


Fig.1: Effect of conc. Of oxidant on yield of Sppy

3.2 Preparation of doped polypyrrole using monomer and oxidant

The yield is given as follows in fig.2 Table no. 3

Sr. No.	Monomer (1M)	Oxidant (1M)	Dopent in (w/v)	Yield in gram	% of Yield
A3	7 ml	14 ml	10 %	0.69 gm	5.86
B3	7 ml	14 ml	20%	0.80 gm	6.41
C3	7 ml	14 ml	30%	1.29 gm	9.70
D3	7 ml	14 ml	40%	2.21 gm	15.90
E3	7 ml	14 ml	50%	3.68 gm	25.5
F3	7 ml	14 ml	60%	4.52 gm	29.60

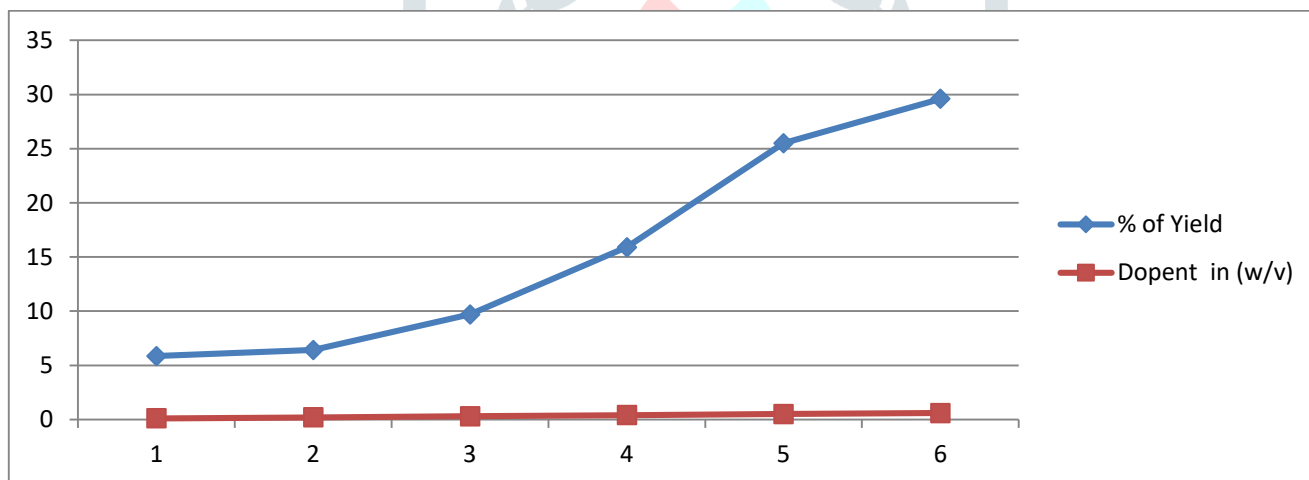


Fig.2: Effect of percentage of dopant (w/v) on yield of doped polypyrrole (using dopent 4-sulfobenzene acid potassium salt).

3.2 Preparation of doped polypyrrole using Monomer and oxidant

The yield is given as follows in fig.3. Table no.4

Sr No.	Monomer	Oxidant	Dopent	Yield	Yield %
A2	7 ml	14 ml	10 %	0.47 gm	3.90
B2	7 ml	14 ml	20%	0.57 gm	4.57
C2	7 ml	14 ml	30%	0.62 gm	4.70
D2	7 ml	14 ml	40%	0. 67 gm	4.83
E2	7 ml	14 ml	50%	0.76 gm	5.21
F2	5 ml	10 ml	60%	0.87 gm	5.89

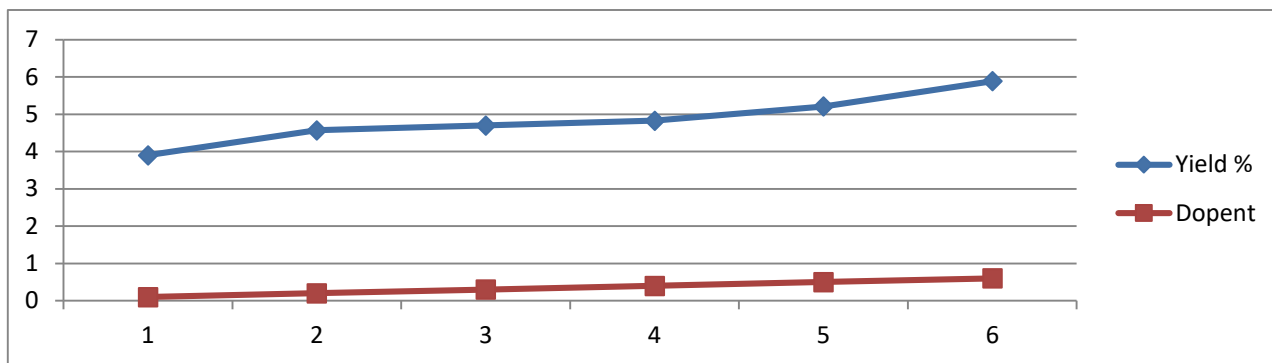
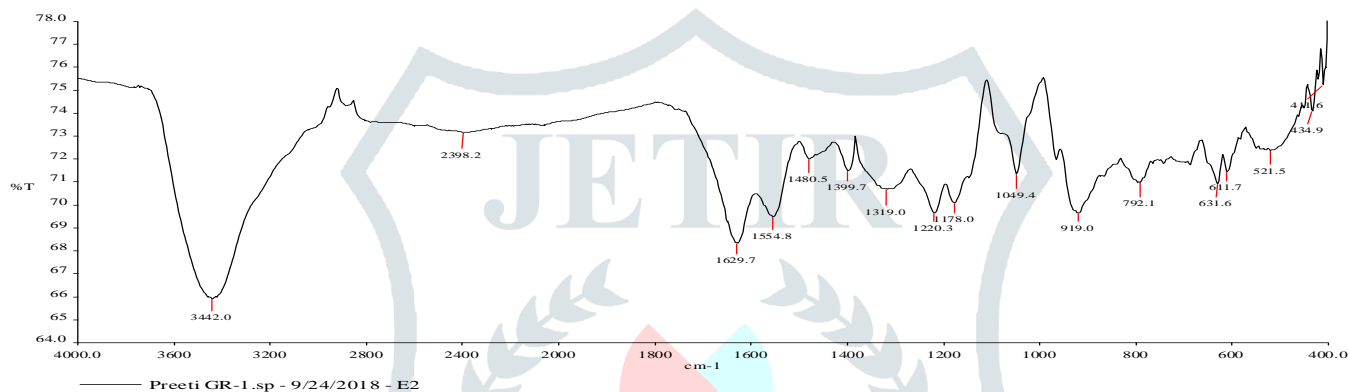


Fig.3: Effect of percentage of dopant (w/v) on yield of doped polypyrrole (using dopent 3- pyridine sulfuric acid).

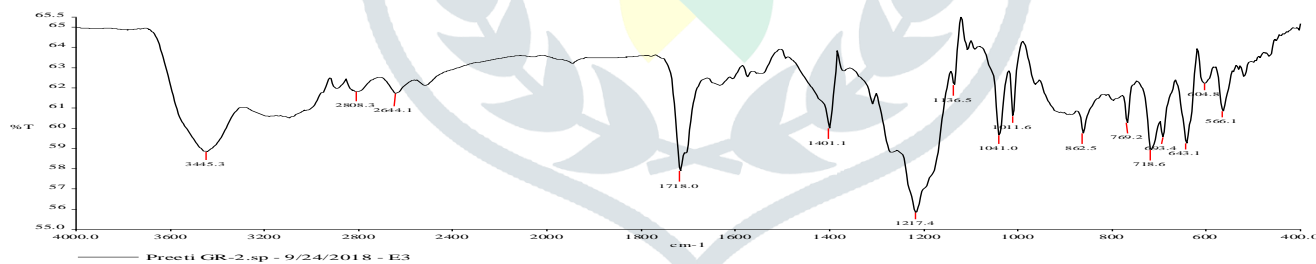
3.4 Fouries transform infrared (FTIR) investigation

The IR studied of undopped polypyrrole 50% w/v in doped PPY/4-SBA potassium salt and 50% w/v doped PPY/3-PSA composites synthesized in present research work are given in FTIR spectra 1,2,3.

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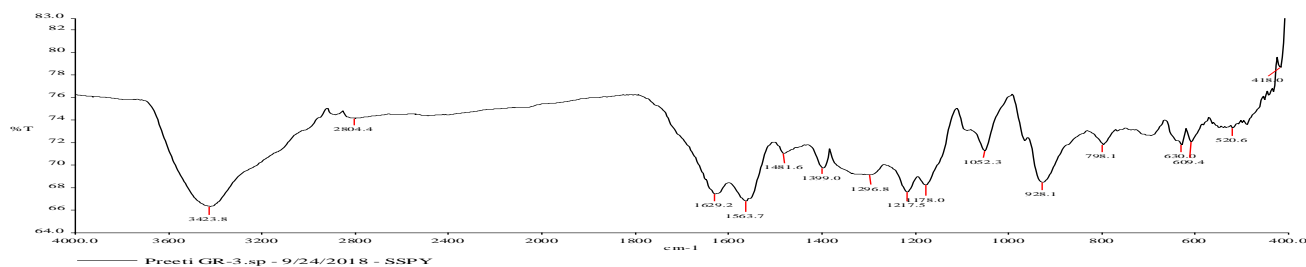


Table 5. :- Vibrational frequencies of FTIR spectra

Polymer composite	Position of absorption maxima (cm ⁻¹)				
	N-H stretching	Ar-H	C=C stretching	C=N stretching	C=C-H bending
Pure PPY (SPPY)	3423.8	2804.4 cm ⁻¹	1563.7 cm ⁻¹	1178 cm ⁻¹	928.1 cm ⁻¹
PPY (E2) 50% doped 3-pyridine sulfuric acid	3442.0	2398.2 cm ⁻¹	1554.8 cm ⁻¹	1178.0 cm ⁻¹	919.0 cm ⁻¹
PPY/ E3 50% doped 4-sulfobenzene acid	3445.3	2808.3 cm ⁻¹ 2644.1 cm ⁻¹	1401.1 cm ⁻¹	1041.0 cm ⁻¹	862.5 cm ⁻¹

The polypyrrole powder prepared in different ways were analysed by FTIR. FTIR spectra showed the main characteristics peaks at 1563.7 cm⁻¹, 1554.8 cm⁻¹, 1401.1 cm⁻¹, corresponding to the fundamental vibrations of polypyrrole ring. These six principle bands are characteristics to represent N-H, Ar-(C=C-H), C=C, C-N, C-C stretching vibration and C=C-H bending vibration respectively. The band at 2804.4 cm⁻¹ correspond to C-H deformation.

Other low intensity peak are observed at around 2398.2 cm⁻¹, 2644.1 cm⁻¹ which can be attributed to aromatic C-H stretching vibration. The peak at 1629.2 cm⁻¹ and 1052.3 cm⁻¹ represents C=N and C-H bonds the bond of C-H in plane deformation vibration is situated at 928.1 cm⁻¹ and of the C-C out of plane ring deformation vibration or C-H rocking is at 681 cm⁻¹ which occur at 693.4 cm⁻¹ in our spectrum. The FT IR spectrum (Fig 1) of the polypyrrole showed charge carries bipolaron bonds at 921.6 and 1207 cm⁻¹ indicating that the PPY formed is in the oxidized state [12,13]. The peaks between 1551 and 1463.8 cm⁻¹ are assigned to fundamental variation of pyrrole rings [14,15]. The peak 3423.8, 3442.0 cm⁻¹ is assigned to N-H stretching vibration from pyrrole in fig 1,2,3. It is observed that the bands obtained a how vibrating frequencies are shift to lower frequency region. This indicated that there is increased in conjugation due to doping which is responsible for vibration in conducting properties of the material.

3.5 NMR spectra of SPPY/ doped PPY

The NMR spectroscopy is an important tool for structural determination of any chemical compound. It easily recognizes the aromaticity and conjugation in the substance. It also gives information of hetroatomic chemical environment.

The NMR studies of SPPY , PPY/3-PBA(E₂) ,PPY/4-SBA(F₃) synthesized in present work are determined by Bruker advanced II NMR spectrometer,SAIF,Panjab university, Chandigarh. The NMR spectra given in the fig.1,2,3 which revealed that NMR spectra of SPPY , PPY/3-PBA , PPY/4-SBA shows three distinct peaks. The first peak is obtained for C=C-H proton at δ 2.5096, 2.5096, 2.5096 in SPPY ,PPY/3-PBA , PPY/4-SBA respectively.The N-H stretching δ is 3.3940,3.5695 in SPPY , PPY/3-PBA respectively.The peak corresponding to aromatic proton is observed that δ 7.1002 in SPPY, (t) 7.1005, (dd) 8.90,(dd) 8.70,(dd) 8.32 indicate that dopant 3-PBA present in the structure. When 4-SBA used as dopant it is observed that no peak at N-H but aromatic hydrogen peak obtained at (t) 7.13 (dd) 7.73,(dd) 7.79 indicate that aromatic compound such as 4-sulfobenoic acid potassium salt used as dopent in it. The increase in δ value of aromatic proton may be due to presence of high concentration of anionic dopant ions in the structure chain after doping . The change in position of aromatic proton may be a consequence which highly affects the conductivity of the sample.

different peaks positions(at 100% intensity) at $2\theta = 17.02^{\circ}$, 25.00° respectively. In addition to the peak shift from 26.24° to 17.02° , Fig. 2 also demonstrates that the peak that formed was sharper than that shown in Fig.1. Furthermore, Fig. 3 shows the peak area at 25° . This finding indicates that the dopants was present in the structure of PPy. The presence of a dopant can generally cause changes in the position and shape of X-ray diffraction peaks. Such changes are caused by corresponding changes in the shape, size and density of the particles examined[24]. However the diffraction peak centered at around 26.24° for pure pyrrole shows some displacement when we go to the doped ones. In general the doping leads to shift the peaks toward the lower angle, being lowest for Ppy doped with 3-PSA (17.02°) and with 4-SBA (25.00°). This indicates that the inter planer spacing increases with the addition of dopants. This would make the chains get apart from each other due to the large sizes of the dopant molecules.

Table:6 X ray Peak Positions of Ppy and with dopants.

Sample	X ray peak position at 100% intensity
Simple Polypyrrole	26.24°
Polypyrrole doped with 3-PSA	17.02°
Polypyrrole Ddoped with 4-SBA	25.00°

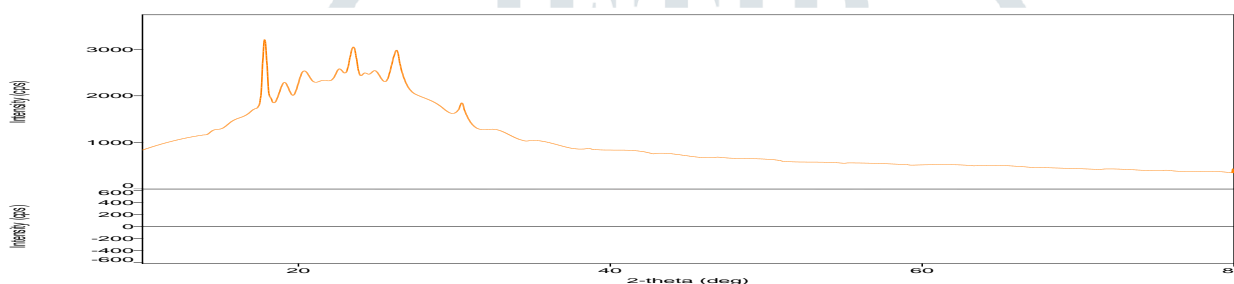


Fig:1: X-ray diffraction patterns of PPy undoped+APS

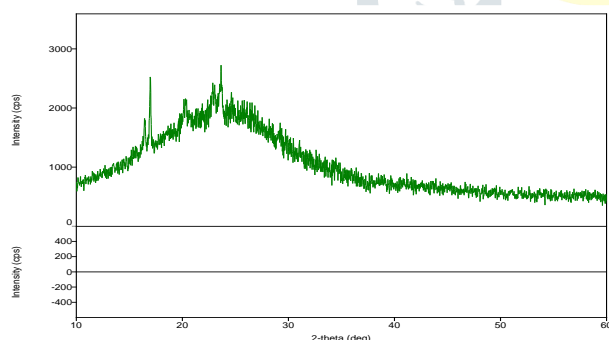


Fig:2: X-ray diffraction patterns of PPy doped PPy/3-PSA

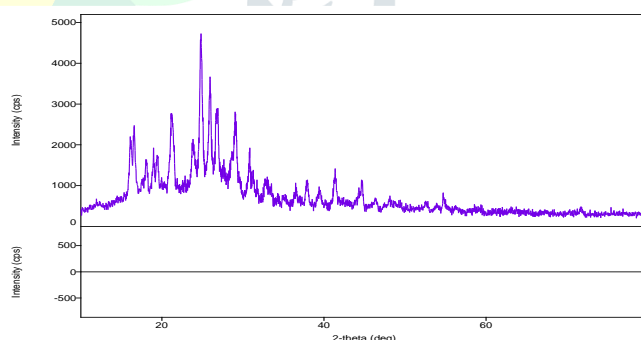


Fig:3: X-ray diffraction patterns of PPy doped 4-SBA potassium salt

3.7 SEM Morphology

The molecule size of PPy was estimated with scanning electron micrographs (SEM).

The SEM micrograph is introduced in Figure 1. Little minimal globular particles of PPy with conveyance measurements in the scope of 5-20 micron were observed. Doped ppy(4-SBA) in the grains are exceptionally agglomerated profoundly sporadic shape a few grains are unpredictable in structure some of them are prolonged and some are round fit as a fiddle.Is presented in fig.2

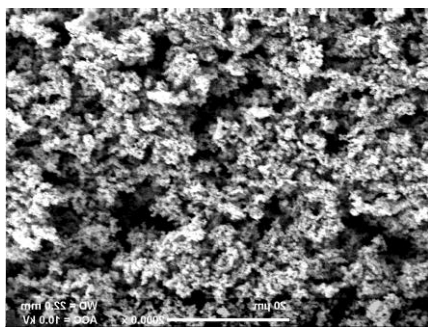


Fig. 1 : SEM micrograph of polypyrrole

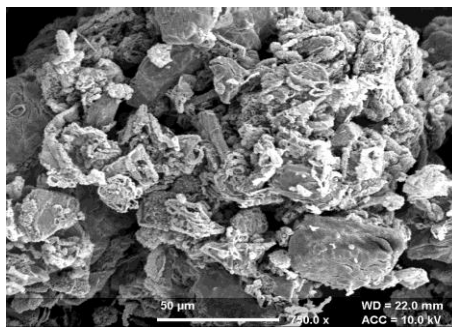


Fig. 2 : SEM micrograph of Doped PPY(4-SBA)

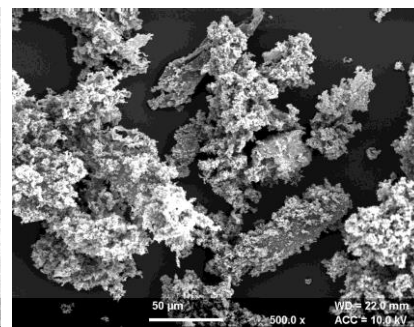


Fig. 3: SEM micrograph of Doped PPY(3-PSA)

When dopants were utilized during the polymerization with APS, the measures of the granules were seen as various. SEM pictures of the PPy particles doped with various dopants of 3- PSA and 4-SBA potassium salt are introduced in SEM picture. It tends to be seen that every convergence of 4-SBA offered ascend to granular PPy particles, in spite of the fact that the molecule size fluctuated with the dopant fixation. The PPy/4-SBA particles are plainly littler than the undoped PPy particles (16). The normal molecule size differed with the surfactant/dopant proportion since this proportion influences the consistency of the arrangement and in light of the fact that the surfactant and dopant likely adsorb onto developing polypyrrole particles [17]. Doped ppy(3-PBA) in which there is development of totals of particles which might be expected to the expanded interchain connection. Is presented in fig.3

4. CONCLUSION

PPY/3-PBA and PPY/4-SBA potassium salt were synthesized at various concentration of dopant. FTIR and NMR imaging confirmed that the dopant used was present in the structure of the polypyrrole particles. It was found that the dopant concentration affected the resulting particles size and also affect conductivity as supported by SEM image . Morphology of thin film were analysed by SEM. It shows change in morphology after doping. XRD spectra demonstrate that amorphous composite polypyrrole particles were formed.

Various factor such as concentration of oxidant and dopant reaction temperature affect on the yield of products. At present work it is observed that increasing molar concentration of oxidant with respective monomer the yield of polypyrrole increases. And also with fix monomer:oxidant ratio 1:2, increasing concentration of dopants yield of polypyrrole increases gradually.

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REFERENCE

1. Jeffries-EL, M., Sauve, G., McCullough, R. *Advanced Materials* 2004, 16, 1017-1019.
2. E. Sezer, V. Erokhin, M.K. Ram and O. Yavuz: *The New Frontiers of Organic and Composite Nanotechnology* edited by E. Sezer, Conducting nanocomposite systems, chapter 4, Elsevier Science, (2007).
3. Gerard M, Chaubey A, Malhotra BD. Application of conducting polymers to biosensors. *Biosens Bioelectron.* 2002 May; 17: 345-359.
4. A. Kassim, Basar ZB, Mahmud HNME. Effects of preparation temperature on the conductivity of polypyrrole conducting polymer. *Proc Indian Acad. Sci. (Chem. Sci.)*. 2002 Apr; 114: 155-162.
5. Ramanaviciene A, Ramanavicius A, *Advanced Biomaterials for Medical Applications*, D. W.s Thomas, Kluwer Academic publishers: Netherlands, 2004; 111-125.
6. Vidal JC, Garcia E, Castillo JR. In situ preparation of a cholesterol biosensor: entrapment Of cholesterol oxidase in an overoxidized polypyrrole film electrodeposited in a flow System. Determination of total cholesterol in serum. *Anal. Chim. Acta*, 1999; 385: 213-222.
7. D, Kamer A, Child AD, Reynold JR. Conductivity Switching in Polypyrrole-Coated Textile

- Fabrics as Gas Sensors Synth. Met. 1998; 92: 53-55.
8. Chougule MA, Pawar SG, Godse PR, Mulik RN, Sen S, Patil VB. Synthesis and Characterization of Polypyrrole (PPy) Thin Films. *Soft Nanosci. Lett.* 2011 Jan; 1: 6-10.
 9. Jerome C, Labaye D, Bodart I, Jerome R. Electrosynthesis of polyacrylic polypyrrole composites: formation of polypyrrole wires. *Synth. Met.* 1999; 101: 3-4.
 10. Smela E, Microfabrication of PPy microactuators and other conjugated polymer de-vices. *J.Micromech. Microeng.* 1999; 9: 1-18.
 9. Kim JH, Sharma AK, Lee YS. Synthesis of polypyrrole and carbon nano-fiber composite for the electrode of electrochemical capacitors *Mater Lett.*, 2006; 60: 1697-1701.
 11. Iroh JO, Williams C. Formation of thermally stable polypyrrol naphthalene/benzenesulfonate carbon fiber composites by an electrochemical process. *Synth Met.* 1999; 99: 1-8.
 12. Tian B & Zerbi G. *J chem. Phys.* 92 (1990) 3892.
 13. Chem A, wang H & Xiaoyu Li, *Chem commun*, (2005) 1863.
 14. Liu J & Wan M. *J poly sci A*, 38 (2000) 2737.
 15. Nguyen T & Diaz A, *Adv Mater*, 6 (1994) 858.
 16. S. Alval,2*, R. S. Utami1, L. K. Shyuan1, I. Puspasari1 and A. B. Mohammad1,3 Synthesis and characterization of toluene sulfuric acid doped polypyrrole nanoparticle: effect of dopant concentration Vol.2 (No.1). 2016. pp.
 17. P. Jayamurgan, V. Ponnuswamy, S. Ashokan, T. Mahalingam, The effect of dopant on structural, thermal and morphological properties of DBSA-doped polypyrrole, *Iranian Polymer Journal*, 22 (2013) 219-225.
 18. Zhang X, Zhang J, Wang R, Zhu T, Lin Z (2004) Surfactant directed polypyrrole/CNT nanocables: synthesis, characterization, and enhanced electrical properties. *Chem Phys Chem* 5:998– 1002.
 19. Oh EJ, Jang KS, MacDiarmid AG (2001) High molecular weight soluble polypyrrole. *Synth Met* 125:267–272
 20. Carrillo I, Sanchez de la Blanca E, Redondo MI, Garcia MV, Gonzalez-Tejera MJ, Fierro JLG, Enciso E (2012) Influence of dopant anions on properties of polypyrrole nano coated poly(styrene-co-methacrylic acid) particles. *Synth Met* 162:136– 142.
 21. B. Akbari, M.P. Tavandashti, M. Zandrahimi, Particle Size Characterization of Nanoparticles–A Practical approach, *Iranian Journal of Materials Science and Engineering*, 8 (2011) 48-56.
 22. J. Hazarika, A. Kumar, Controllable synthesis and characterization of polypyrrole nanoparticles in sodium dodecylsulphate (SDS) micellar solutions, *Synthetic Metals*, 17 (2013) 155-162.
 23. C. MA, S. Shashwati, Synthesis and characterization of polypyrrole (PPy) thin films, *Soft Nanoscience Letters*, 2011 (2011).
 24. H.K. Chitte, N.V. Bhat, A.V. Gore, G.N. Shind, Synthesis of Polypyrrole Using Ammonium Peroxy Disulfate (APS) as Oxidant Together with Some Dopants for Use in Gas Sensors, *Materials Sciences & Applications*, 2 (2011).