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"SYNTHESIS AND CHARACTERIZATION OF POLY (ANILINE CO- M- NITRO ANILINE) DOPED WITH INORGANIC ACIDS."

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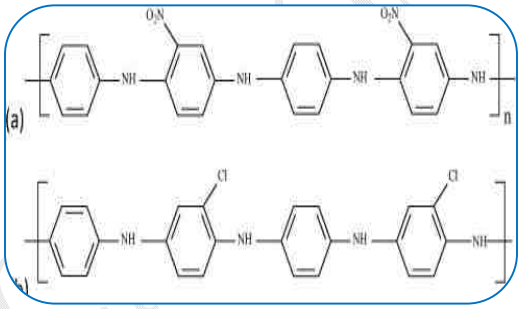
ABSTRACT :

*Present work reports synthesis and characterization of poly (aniline c**o- m**eta nitro aniline) by using various mineral acids. Poly(aniline co- meta nitro aniline) was synthesized by chemical oxidative polymerization of monomer aniline and co monomer meta nitro aniline at room tempreture.Hydrochloric acid,sulphuric acid and perchloric acid were used as a dopent along with acrylic acid as a soft templet. Synthesized Poly (aniline co - meta nitro aniline) was characterized by analytical techniques such as FTIR,UV-DRS and XRD.*



KEYWORDS : *Oxidative polymerization, dopant, mineral acid and soft templet.*

INTRODUCTION:

1.1 POLYMERS :

A Polymer is a large molecule, or macromolecule, composed of many repeated subunits, known as monomers. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness,

1.2 POLYANILINE:

Polyaniline (PANI) is polymer of the semi – flexible rod polymer family. Although the compound itself was discoursed over 150 years ago, only since the early 1980s has polyaniline captured the intense attention of the scientific community. This interest is due to the rediscovery of high electrical conductivity. Amongst the family of conducting polymers and organic semiconductors, Polyniline has many attractive processing properties. Because of its rich chemistry, Polyaniline is one of the most studied conducting polymers of the past 50 years. Polyaniline (PANI) exists in a variety of forms that differ in chemical physical properties.

The most common green protonedemeraldine has conductivity on a semiconductor level of the order of 100s cm-1, many orders of magnitude higher than that of common polymers (<e.g. 10^{-9} S cm-1) but lower than that of typical metals (>10^{-4} S cm-1) . protonated PANI, (e.g. PANI hydrochioride) converts to anonconducting blue emeraldine base when treated with ammonium hydroxide-

Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to Polyaniline (emeraldine) base. It is an arbitrary anion, e.g. chloride.

Synthesis and Properties :

Polymerized from the inexpensive aniline monomer, poluaniline can be found in one of three idealized oxidation states:

A) **Emeraldine**Green for the emeraldine salt, blue for the emeraldine base ({$[C_6H_4NH]_2[C_6H_4N]_2$}n)
B) **(Per) nigraniline** – blue /violet $(C_6H_4N)_n$Leucoemeraldine with n= 1, m= 0 is the fully reduced state. Pernigraniline is the fully oxidized state (n=0, m= 1) with links instead of amine links. Studies have shown that most forms of polyaniline are one of the three states or physical mixtures of these components. The emeraldine (n = m= 0.5) form of polyaniline, often referred to as emeraldine bas (EB), is neutral, if doped (protonated) it is called emeraldine salt (ES), with the iminenitrogensprotoned by an acid. Protonation helps to delocalize as the most useful form of diiminoquinone-diaminobenzene state. Emeraldine base isregarded as the most useful form of polyaniline due to its high stability at room temperature and the fact that, upon doping with acid, the resulting emeraldinesaltform of polyaniline is highly electrically conducting.Leucoemraldine and pernigraniline are poor conductors, even when doped with an acid. The efficient polymerization of aniline ia achieved only in an acidic medium, whereaniline exists as an aniliniumcation. A variety of inorganic and organic acids of different concentration have been used in the synthesis of PANI; the resulting PANI; protonated with various acids, differs in solubility, conductivity, and stability. The colour change associated with polyaniline in different oxidation states ordoping levels. Treatment of emeraldine with acids increase the electrical conductivity by ten ordes of magnitude. The same material can be prepared by oxidation of leucoemeraldine. The handling of solid aniline salt is preferred by oxidation of leucoemeraldine. The handling of solid aniline salt is preferred to liquidaniline from the point of view of toxic hazards.

To minimize the presence of residualaniline and to abtain the best yield of PANI, the stoichiometricperoxydisulfate/anilineratio 1.25 is recommended. Polyaniline is nobler than copper and slightly less noble than silver which is the basisforits broad use in printed circuit board manufacturing (as a final finish) and in corrosion protection.

- **Characteristics of Polyaniline :**

Polyaniline of higher molar mass is produced at lower reaction temperatures, but the electrical properties of the polymer are not greatly influenced by molar mass. We have selected ambient temperature for the present study while being aware of the ambiguous definition of such conditions. As temperature increase during there action, this increase being dependant on the surface – to- volume ratio of the experimental set – up, the precise control of temperature was not attempted. The effect of reaction temperature on the conductivity of PANI was assessed and is discussed. Polymerization in the presence of excess HCL, i.e. at higher activity.

- **General applications of Polyaniline :-**

Polyaniline and the other conducting polymers such as polythiophene, polypyrrole, and PEDOT/PSS have potential for applications due to their light weight, conductivity, mechanical flexibility and low cost. Polyaniline is especially attractive because it is relatively inexpensive, has three distinct oxidation states with different colors and has an acid/base doping response. This latter property makes polyaniline an attractive for acid/base chemical vapour sensors, super capacitors and biosensors. The different colors, charges and conformations of the multiple oxidation states also make material promising for applications such as super capacitors and electrochromics. They are suitable for manufacture of electrically conducting yarns, antistatic coatings, electromagnetis shielding, and flexible electrodes. Attractive fields for current and potential utilization of polyaniline is in antistatics, charge dissipation or electrostatic dispersive (ESD) coating and blends, electromagnetic interference shielding (EMI), anticorrosive coating, hole injection layers, transparent conductors, indium tin oxide

replacements, actuators, chemical vapour and solution based sensors, electrochromic coating (for color change windows, mirrors etc.), PEDOT-PSS replacements, toxic metal recovery, catalysis, fuel cells and active electronic components such as for non-volatile memory.

1.3 Copolymerization:-

Copolymerization is a process when on like molecules join together in random sequence or alternating sequences.

For example : copolymer of online with m-nitroaniline [poly (aniline-co-m-nitroaniline)] were readily synthesized in various molar ratios of comonomers by chemical and electrochemical polymerization rate decreased with an increasing ratio of m-nitroaniline in monomer (Ding et al.jzolz)

Chemically oxidative copolymerization of aniline & o-chloroaniline with 4m ratios has been performed using ammonium persulphate as an oxidant in HCl medium at 0-4°C (Broker, 2012) showed structure of copolymer.

MATERIALS AND METHODS

3.1 CHEMICALS:

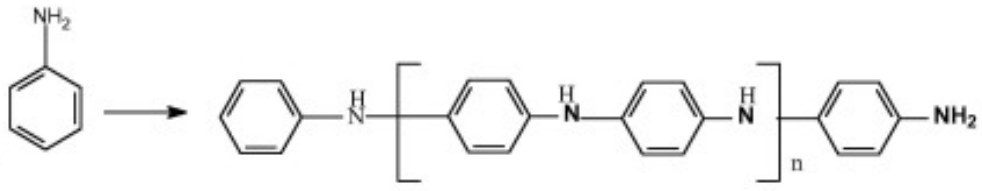
All chemical used were of A.R grade and used without further purification.

1. APS(Ammonium Per Sulphate),(Qualigen)
2. Concentrated HCl (Hydrochloric acid),H_2SO_4 (Sulphuric acid),$HClO_4$ (Perchloric acid)
3. Distilled water
4. Aniline, (Qualigen)
5. Acrylic acid, (S.D.Fine)

Aniline was distilled before use

3.2 Synthesis of Polyaniline:

For the synthesis of Polyaniline, 1ml of aniline (monomer solution) was taken in a beaker and 2ml of concentrated hydrochloric acid was added to it.30ml of distilled water was introduced to it which was kept in ice bath to maintain a temperature at about 0-5^{0}C. This whole assembly was kept on magnetic stirrer for stirring. 1ml of arylic acid was added further.1.14gm of APS was dissolved in 10ml distilled water and addeddropwise to the above solution. Conc.HCl was added in this reaction mixture acts as dopant. Reaction was carried out for half an hour at 0-5^{0}C. The reaction was carried out till green colour appears indicating the formation of Polyaniline.

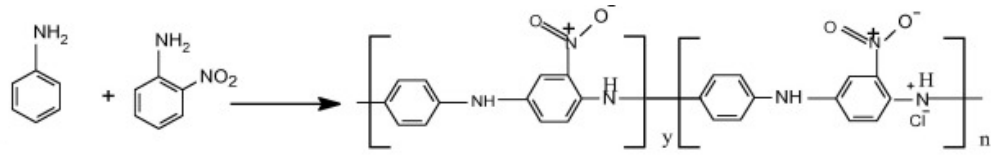


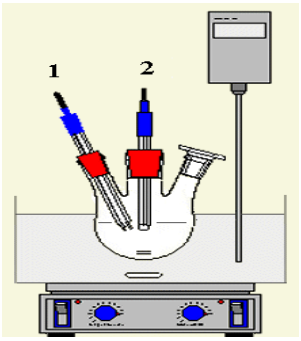
3.2 Synthesis of poly (aniline-Co-m-nitroaniline)

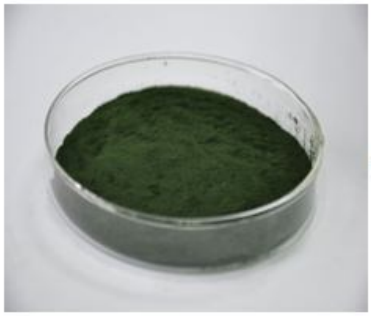
In the case of the preparation of poly (aniline-Co-m-nitroaniline), 1.8ml Aniline, and 2ml conc.hcl or conc.H2SO4 was dissolved in 100 ml distilled water.

Then 1ml acrylic acid was added to it dropwise. 2.28gm APS dissolved in 5ml H2O & added dropwised to above solution. The solution turns white initially and later turns into deep blue colour. Then 0.266 gm m-Nitroanilineadd to above solution. Dilute upto 200ml by distilled water. The solution was precooled at 0^{0}C. also the whole reaction is carried out at temperature 0-5^{0}C.

The reaction mixture was stirred continously on magnetic stirrer using magnetic needle for about 3hour to abtain the product which is deep green in colour and further analysed for its conformation using various analytical technique.







UV

FTIR

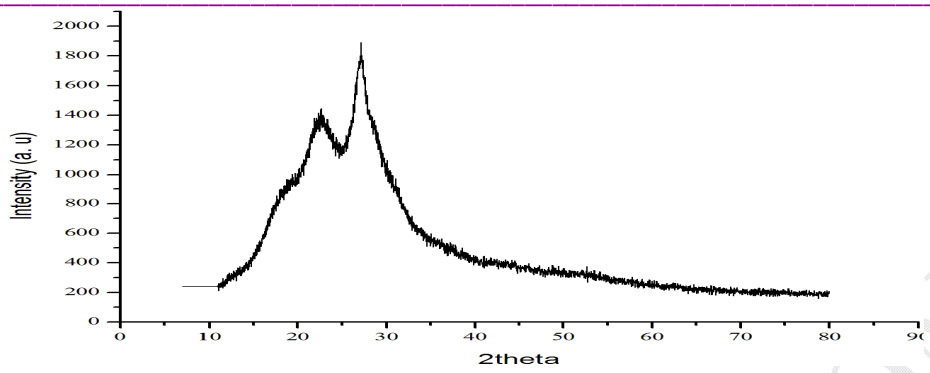
XRD

SEM

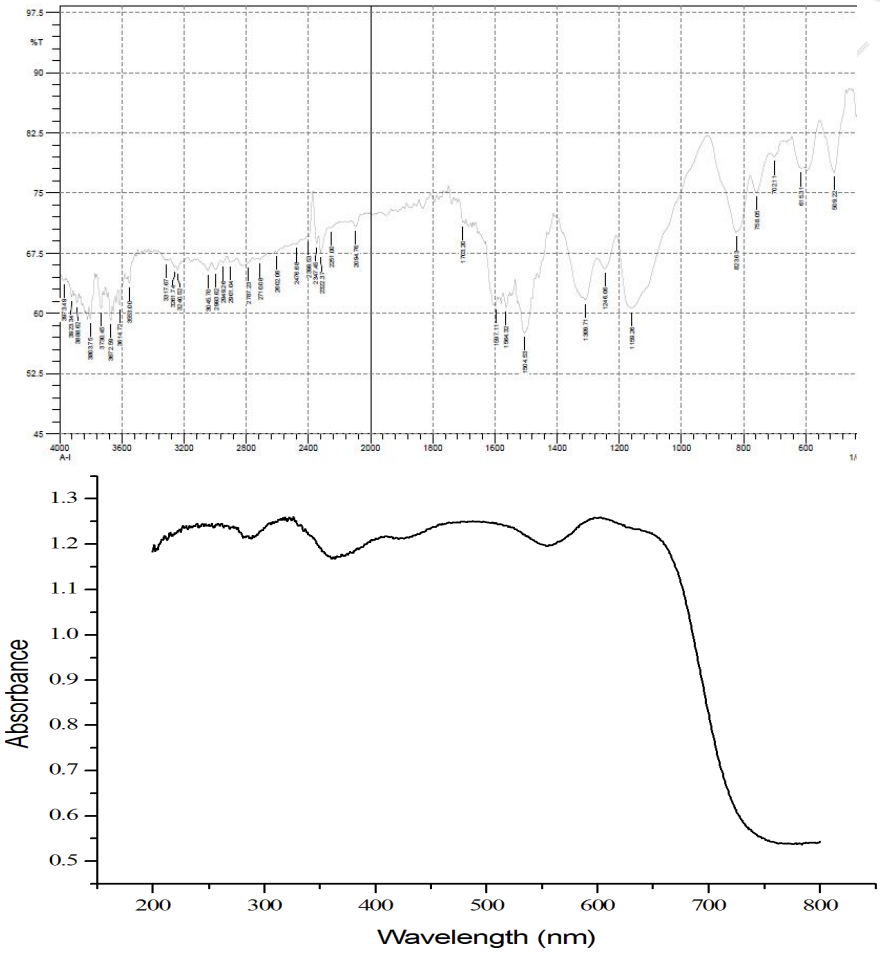
TGA

RESULTS AND DISCUSSION

Polymer	Soft Templet	Monomer	Co-monomer	Dopant	Yield(%)
Poly(aniline co –m-nitroaniline)	Acrylic Acid	1:0:1	0-5^{0C}	HCl	90
				H_2SO_4	88
				$HClO_4$	85
		1:0:2	RT	HCl	57
				H_2SO_4	50
				$HClO_4$	45

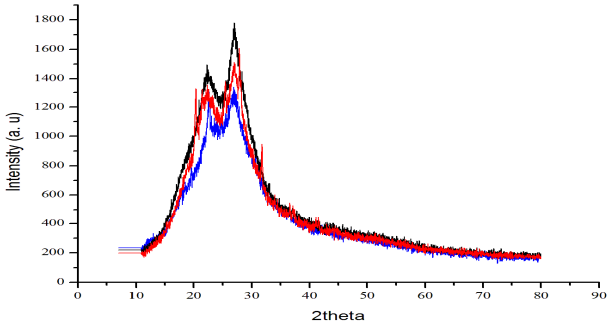


The XRD patterns of PAni shown in figure indicates that PANI synthesized by mineral acid dopant has crystalline in nature.

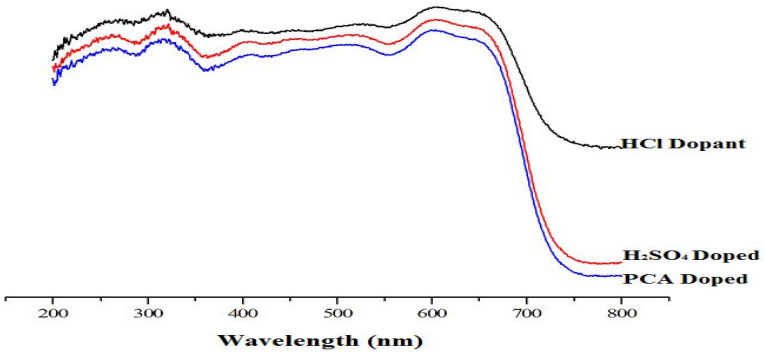


UV DRS Spectra of PANI shows that band gap of material is less than 9ev which confirms its conducting nature .

Characterization of synthesized Poly (aniline co-meta nitro aniline



XRD patterns of Poly (aniline co meta nitro aniline) by using three different mineral acid.



UV DRS images of poly (aniline co meta nitro aniline.

CONCLUSION

Polyaniline and co metanitroaniline can be synthesized by oxidative polymerization method.Morphology of polymer material was not affected by dopantused.Polymerisation reaction rate was affected by tempreture.HCl doped polymer has less band gap than the H_2SO_4 doped polymer while $HClO_4$ doped polymers shows large band gap. .Hence HCl doped polymers shows good conductivity than other acid dopant. Use of templet on conductivity.

REFERENCES

1. V. V. Chabukswar; S. Pethkar; A. A. Athwale, Acrylic acid doped polyaniline as an ammonia sensor, Sensors and Actuators B77 (2001) 657-663.
2. A. Mekki, N. Joshi, A. Singh, Z. Salmi, P. Jha, P. Decorse, S. L. Troung, R. Mahmoud, M. M. Chehimi, D. K. Aswal, S. K. Gupta, Org.Electr., 2014, 15, 71.
3. 3.S. Sathiyanarayanam; S. Muthkrishnan; G.Venkatachari, ElectrochimActa 2006,51,6313.
4. S. K. Dhawan; D. Kumar; M. K. Ram; S. Chandra; D. C. Trivedi, Application of conducting polyaniline as sensor material for ammonia, Sensor and Actuators B, 40 (1997) 99-103

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