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Aromatic Tri-Carboxylic Acid Doped Polyaniline Nanostructure: Synthesis And Spectral Properties

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Abstract: *Polyaniline (PANI) is a very good conducting polymer among the conducting polymer family. Advantage of PANI is easy to synthesis, low-cost, special proton doped mechanism, as well as physical properties controlled by both oxidation and protonation state. The conduction of PANI mainly depends on the nature of the dopant acids which is essential for PANI preparation.*

PANI nanostructure have been synthesized by in-situ polymerization technique using isomeric benzene tricarboxylic acid (1,2,3; 1,2,4 and 1,3,5; dopant acids) and APS as a oxidizing agent. Characterization of the composite was done with the help of UV-Vis, FT-IR, XRD, ^{1}H-NMR, optical microscopy and HRTEM images. Here we have used the same acid functionality isomeric acid but different position of the acid group for evaluation of the effect of geometrical arrangement of the dopant in polyaniline nanostructure particularly nanofibers. For investigation of the mechanism of fiber formation, saturated analogue of tricarboxylic acid (cyclohexane tricarboxylic acid) having same functionality has been used. With different ratio of [acid/[ani], PANI have been prepared to check the property of PANI on the different ratio of the [acid]/[ani]. Being motivated by the result, PANI using poly-nuclear aromatic tri-carboxylic acid has been synthesized to understand the effect of size of the dopant acid in PANI nanofibers.

Keywords: *Polyaniline, Doping, Nanostructure, Conducting Polymer, Morphology.*

Introduction: Plastics are typical organic polymers with saturated macromolecules and are generally known as excellent electrical insulators. But interestingly some conducting polymers have been discovered like polyacetylene, polypyrrole, polythiophene, polyaniline. According to electrical properties, materials can be divided into four types: insulator, semiconductor, conductor, superconductor. In general, a material with aconductivity less than 10^{-7} S/cm is regarded as an insulator. A material with conductivity larger than 10^{-3} S/cm is called as a metal whereas the conductivity of a semiconductor is in a range of 10^{-4}-10 S/cm depending upon doping degree.

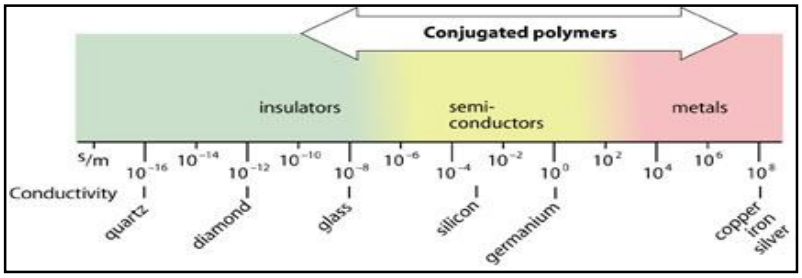
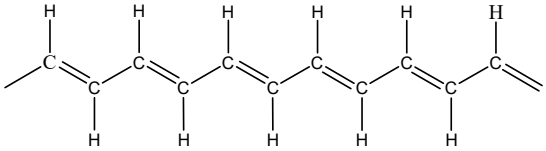


Fig :1 Conductivity of conducting polymers can cover whole insulator- semiconductor- metal region by changing doping degree [18]

Organic polymers usually are described by σ bonds and π bonds. The σ bonds are fixed and immobile due to forming the covalent bonds between the carbon atoms. On the other hand, the π electrons in conjugated polymers are relatively localized, unlike the σ electrons. Since discovery of conductive polyacelene (PA) doped with iodine, [9] a new field of conducting polymers, which is also called as "synthetic metals", has been established. Polymers containing π bonds are usually conducting in nature. In the 1960s-1970s, a breakthrough, polymer becoming electrically conductive, was coming out. The breakthrough implied that a polymer has to imitate a metal, which means that electrons in polymers need to be free to move and not bound to the atoms. In principle, an oxidation or reduction process is often accompanied with adding or withdrawing of electrons, suggesting an electron can be removed from a material through oxidation or introduced into a material through reduction. Above idea implies that a polymer might be electrically conductive by withdrawing electron through oxidation (hole) or by adding electron through reduction, which process was latterly described by an item of 'doping'. The breakthrough was realized by three Nobel laureate in 2000, who were Alan J. Heeger, Alan G. MacDiramid, Hideki Shirakawa,[10] they accidentally discovered that insulating π-conjugated Polyacelene could become conductor.



Molecular structure of polyacetylene

In another part of the world, Alan G. MacDiramid and Physicist Alan J. Heeger at University of Pennsylvania, Philadelphia, USA were studing the first metal-like inorganic polymer sulphur nitride ($(SN)_x$), which is the first example of a covalent polymer without metal atom [11] **Polyaniline** (**PANI**) is a conducting polymer of the semi-flexible rod polymer family. Although the compound itself was discovered over 150 years ago (in the year 1862, known as "Aniline black"**)** **[1],** only since the early 1980s has polyaniline captured the intense attention of the scientific community. "Aniline black" was prepared from the anodic oxidation of aniline and accompanied a colour change upon switching potential,which latterly was called as electrochromism [12]. However, it was regret that the electrical properties were not measured at that time! In 1985, MacDiramid for the first time, found that aniline monomer in an acid aqueous solution can be chemically oxidized by ammonium peroxydisulphate (APS) to obtain green powder of PANI with a conductivity of as high as 3 S/cm, as measured by four-prob methods, which results were published in 1986. [13] Amongst the family of conducting polymers and organic semiconductors, polyaniline 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 remains of widespread interest,[14] providing an opportunity to address fundamental issues of importance to condensed matter physics, including, for example, the metal-insulator transition,[15] the Peierls Instability and quantum decoherence.[16] Using special polymerization procedures and surfactant dopants, the polyaniline powder can be recovered after polymerization can be made dispersible and hence useful for practical applications. Bulk synthesis of polyaniline nanofibers has led to a highly scalable and commercially applicable form of polyaniline that has been researched extensively since their discovery in 2002.[17] Synthesis of PANI with di-carboxylic acid[19] and tetra-carboxylic acid [3] was reported earlier.

Polyaniline (PANI) is an important conducting polymer due to its easy polymerization procedure, good chemical stability, convenient acid doping process and high conductivity. Depending on the morphology and electronic state of PANI it is used in chemical and biological sensors, gas separation membranes, electronic devices, light weight battery electrodes, anticorrosion coatings, etc. Synthesis of polyaniline nanostructures are great interest in polymer research because it can be used to enhance sensor properties due to its large surface area and low dimensional conductivity.

Our target is to make the polyaniline nanostructure using the aromatic tricaroboxylic acid by *insitu* polymerization technique. For these purpose we have used three types of isomeric benzene tricarboxylic

acid,(1,2,3; 1,2,4 and 1,3,5) as a dopant acids that is essential for PANI nanostructure formation. For better understanding the effect aromatic core on nanostructure we also used cyclohexane tricarboxylic acid as a dopant having the same acid functionality but saturated instead of unsaturated acid. We also try to tuning the property of PANI by changing the [acid] / [ani.] ratio. Being motivated by the result we also continue to synthesize PANI using poly-nuclear aromatic tri-carboxylic acid.

Experimental

Chemicals: Aniline monomer (Merck Chemicals) was distilled under reduced pressure prior to use. Benzene-1,2,4-tricarboxylic acid (BTA-2), Benzene-1,2,3-tricarboxylic acid (BTA-3) was purchased from Alfa Aesar and Cyclohexane-1,3,5-tricarboxylic acid (CTA) and Benzene-1,3,5-tricarboxylicacid (BTA-1) from Sigma-Aldrich and used without purification. Ammonium persulphate was purchased from Merck Chemicals and used without any purification. Biphenyl-3,5,4'-tricarboxylicacid(BPTA) and 1,3,5-tris(4-carboxyphenyl) benzene (TPTA) were taken from Mr. Pradip Kumar Sukul, my lab-senior, who synthesized those.

Spectroscopic measurements: UV-Visible spectroscopy was done using Agilent (model no.8453) UV-Vis spectrophotometer in 1.0 cm path length cell. The FTIR spectra were scanned at Perkin Elmer Spectrum 100 FTIR-Spectrophotometer using the KBr pellets of the samples. ^{1}H NMR spectral readings were taken from 500 MHz Bruker NMR instrument.

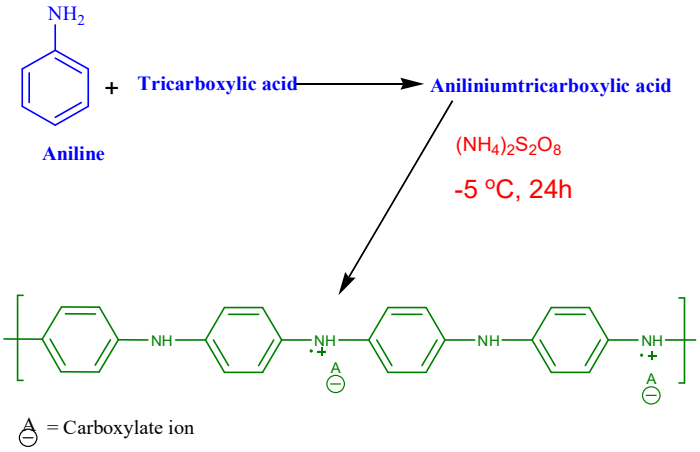
Microscopy of the samples: For optical microscopy the sample was cast on glass slide from the mother solution and was dried at room temperature and seen in Olympus BX51 optical microscope with the help of ProgRes Capture Pro 2.7 software. HRTEM (JEOL, 2010 EX) investigation was carried out by spreading the sample on Cu-grid coated with holey carbon support film and micrographs were taken at an accelerating voltage of 200 kV fitted with a CCD camera.

Structural measurement: XRD of the all powder samples were measured using a Bruker AXS diffractiometer (D8 advance) using Cu Kα radiation (λ=1.54 A°), a generator voltage 40 kV and current 40 mA. Samples were scanned in the range of 2θ=5°-40°.

Synthesis: Polyaniline is prepared from anilinium ion, prepared using tri-carboxylic acid in water, followed by oxidation using APS by in-situ polymerization technique.

At first measured amount of tri-carboxylic acid was dissolved in 15ml distilled water, 0.1ml aniline was added and the mixture was stirred for 1 hour at room temperature. The resulting mixture was allowed to cool at 12^0 C. Then solution of ammonium persulphate(APS), prepared by dissolving required amount of APS in 5ml water, added slowly over 30 minutes to the cool mixture with continuous stirring. The final mixture was then allowed to stand at 0^0 to -5 ^{0}C for 24 hours. The green colored product was then filtered and washed several times with methanol and water until colorless, then dried in vacuum oven for overnight.

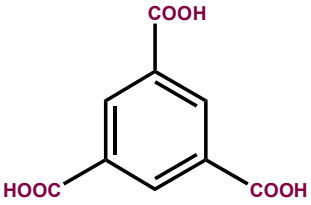
Schematic:



Emeraldine salt (ES) form of polyaniline

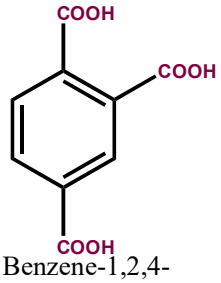
Synthesis Using Isomeric Benzene Tri-Carboxylic Acid

The acids used for this purpose as a dopant for making the PANI nanostructure-



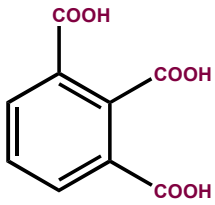
Benzene-1,3,5-tricarboxylic acid

BTA-1



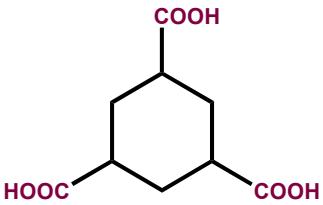
Benzene-1,2,4-tricarboxylic acid

BTA-2



Benzene-1,2,3-tricarboxylic acid

BTA-3



Cyclohexane-1,3,5-tricarboxylicacid

CTA

The mole ratio and amounts of the compound used are given

Table: 1

NAME	Mol. Weight	Wt. taken(mg)	mmol conc.	Mole ratio
Aniline	93	94.86	1.02	-----
BTA-1	210	54.68	0.26	[BTA-1]:[ani.]=0.25:1
BTA-2	210	54.76	0.26	[BTA-2]:[ani.]=0.25:1
BTA-3	210	54.62	0.26	[BTA-3]:[ani.]=0.25:1
CTA	216.19	56.24	0.26	[CTA]:[ani.]=0.25:1
APS	228	232.56	1.02	[APS]:[ani.]=1:1

COMPOSITE	BTA-1 PANI	BTA-2 PANI	BTA-3 PANI	CTA-PANI
YIELD(mg)	69.72	82.83	73.95	70.84

Characterization:

Characterization by UV-vis. Spectroscopy: UV –Vis. Spectroscopy was done in DMSO and water.

UV-Vis. Study in DMSO : UV spectra of PANI in DMSO shows two peaks. The peak position around 325 nm ascribes to π-π* in the benzenoid rings and at 630 nm for polaron- π transition of PANI are the characteristics peaks of polyaniline.

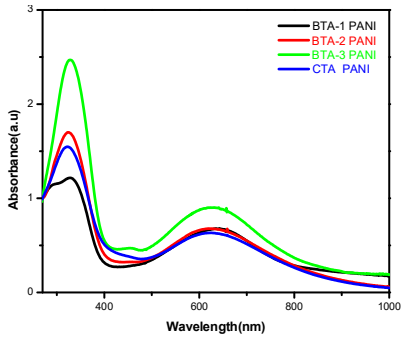


Fig-2: UV-Vis spectroscopy of different PANI-acid composites in DMSO.

UV-Vis. Study in water: 0.5 mg of the PANI sample was dispersed in 2.5 ml water for UV-Vis spectroscopic study. Three bands arise at ~350nm, ~450 nm and ~910 nm which ascribe for π-π*, polaron-π* and polaron-π transition respectively.

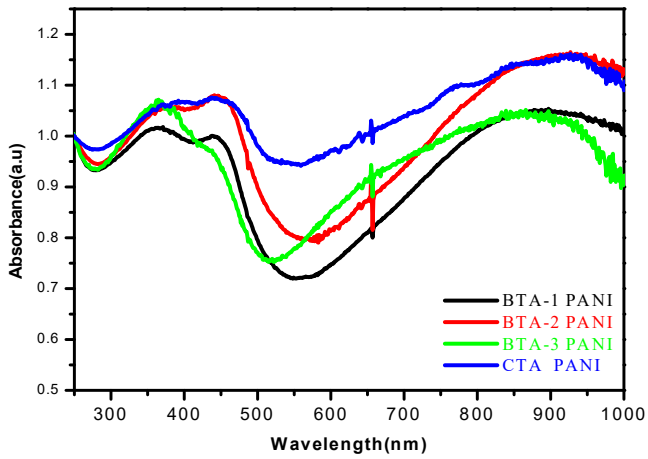


Fig-3: UV-Vis spectroscopy of different PANI-acid composites in water medium

Characterization by FTIR spectroscopy: In order to prove the formation of PANI in the composites, the FTIR studies of different PANI-acid composites were performed. The presence of stretching bands near 1580, 1480, 1295, 1100, 785 cm^{-1} reveals the formation of PANI.

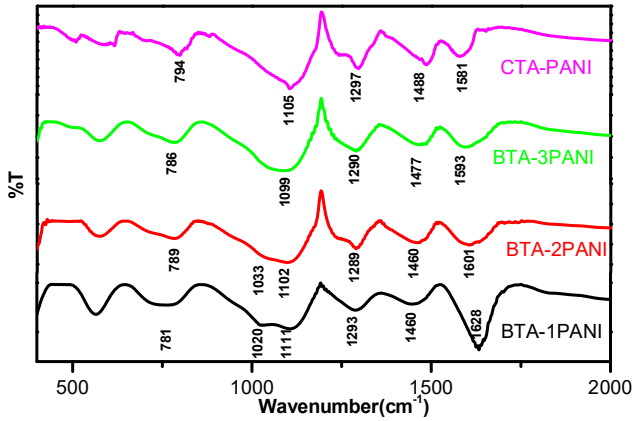


Fig-4: FTIR spectra of different PANI-acid composites

Table: 2

Composites	Bands appeared (cm^{-1})					
	C=C quinoid	C=C benzenoid	C-N secondary amine str.	In plane C-H deformation	Doping of PANI with acid	Out of plane C-H deformation
CTA-PANI	1581	1488	1297	1105		794
BTA3-PANI	1593	1477	1290	1099	Broad peak	786
BTA2-PANI	1601	1460	1289	1102	1033	789
BTA1-PANI	1628	1460	1293	1111	1020	781

C-N secondary amine band appears for π electron delocalization. [3,4,5]

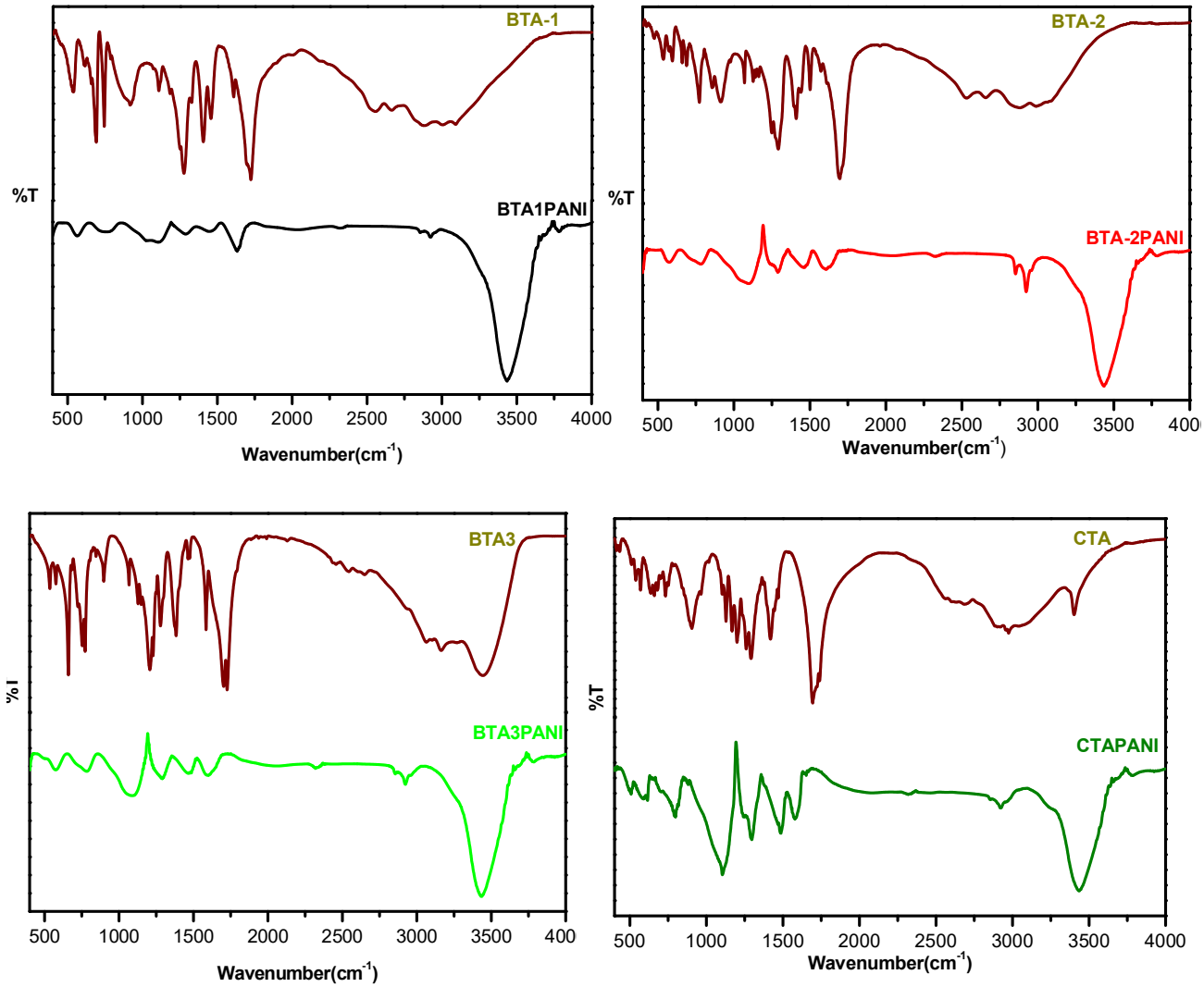
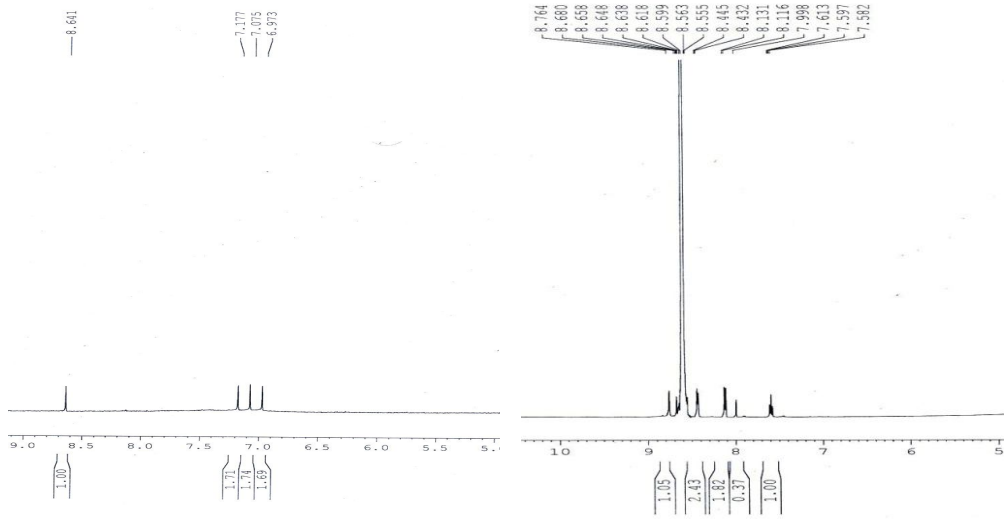


Fig5. FTIR spectra of different PANI-acid composites with the corresponding acid

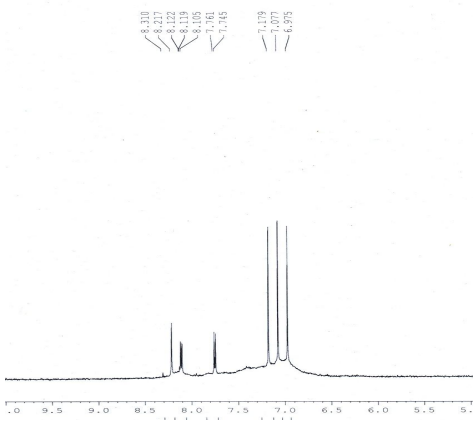
Characterisation by FT-NMR (1H) spectroscopy: (^{1}H,500MHz,DMSO-d_6)



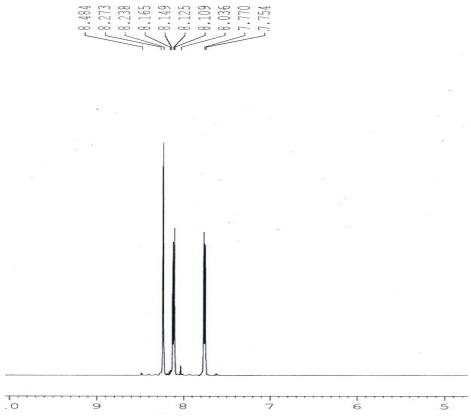
BTA-1 PANI **BTA-1**

The ^{1}H spectra of BTA-1 PANI shows three sharp, equal-strength, equidistance peaks at δ=6.973, 7.075, 7.177 with a coupling constant of 51 Hz. This type of triplet peaks could not be attributed to the aromatic proton as they usually display a triplet with an integral area ratio of 1:2:1. The equal strength triplet could

only be attributed to the proton related to nitrogen, since the ^{14}N atom has spin quqntum number I_N =1 which makes it possible for the proton on ^{14}N to exhibit the triplet peaks with an integral area ratio of 1:1:1[2,6,7]. The peak position 8.64 for the BTA in PANI chain indicates that the our synthesized polyaniline highly doped by BTA.

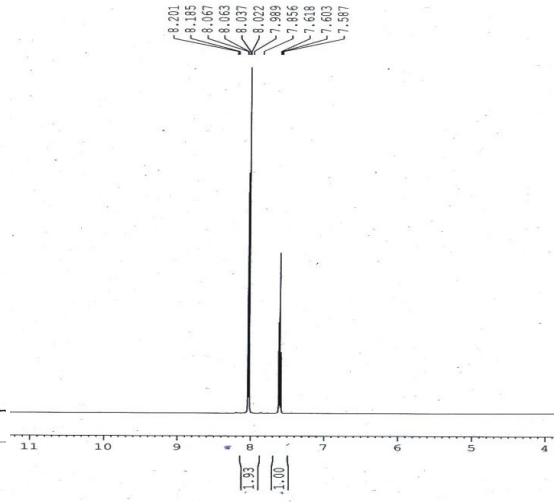


BTA-2 PANI

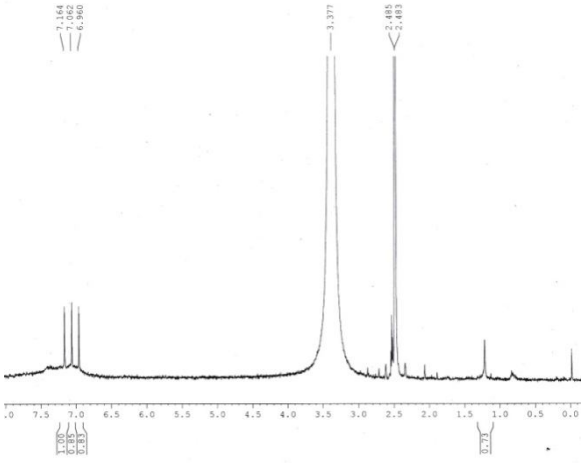


BTA-2

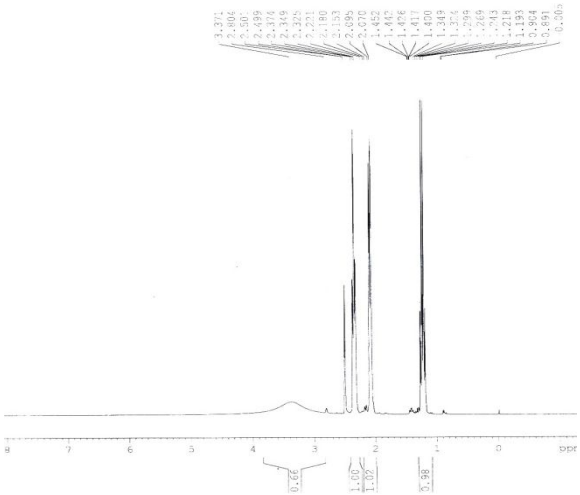
BTA3-PANI



BTA3



CTA PANI



CTA

The peaks positons of polymers in BTA-2 PANI, BTA-3 PANI, CTA PANI are same as like BTA-1 PANI.

Characterization by XRD Analysis: To judge the crystallinity of PANI /BTA composites, X-ray diffraction was performed. Three peaks arises for BTA-1 PANI at 2θ=8.69°, 16.3°, 20.61° and 25.60°.Peak at 25.60° due to periodicity in the direction perpendicular to the polymer chain. The d-spacing (3.48Å) associated with the diffraction peak at 25.60° corresponds to the face to face inter chain stacking distance between phenyl rings. High intensity at this position implies improved π-π inter chain stacking. Peak at 20.61° ascribes periodicity in the direction parallel to the PANI chain. Peak at 8.60 is due to repeat unit of PANI chain[9] and the peak at 16.3 due to crystallinity[8]. The above peaks also arises in BTA-3 PANI composite at 25.52°, 20.87°, 16.04° and8.56°.

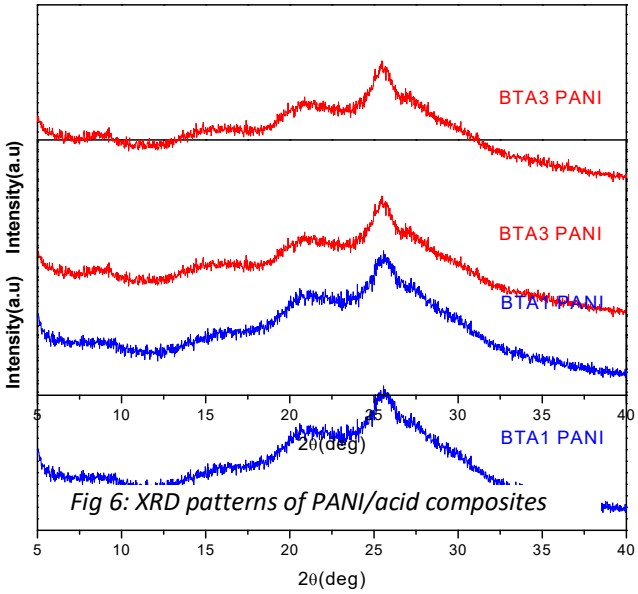


Fig 6: XRD patterns of PANI/acid composites

Judging from the difference in contrast between the edge and the core of fibres in the HRTEM images of BTA-1 PANI /BTA composite,it is clearly showing formation of nanotubes

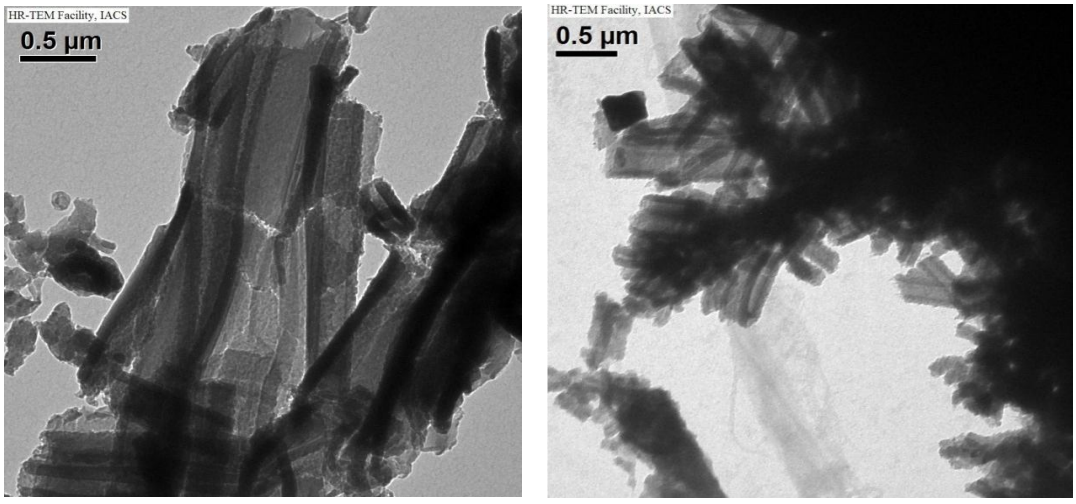


Fig 7: HRTEM images of BTA-1/BTA-1 PANI composites conform the formation of PANI nanotubes

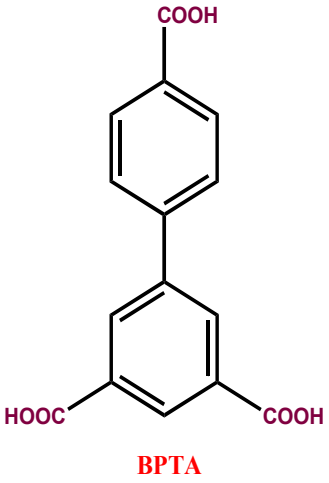
Synthesis Using Polynuclear Aromatic Tri-Carboxylic Acid

The experiment is also continued to see the effect of number of benzene ring in the tri-carboxylic acid on the properties PANI.For this purpose BPTA and TPTA are used as dopant.In simple optical microscopy image very clear fibre like morphology was observed.

Table: 3

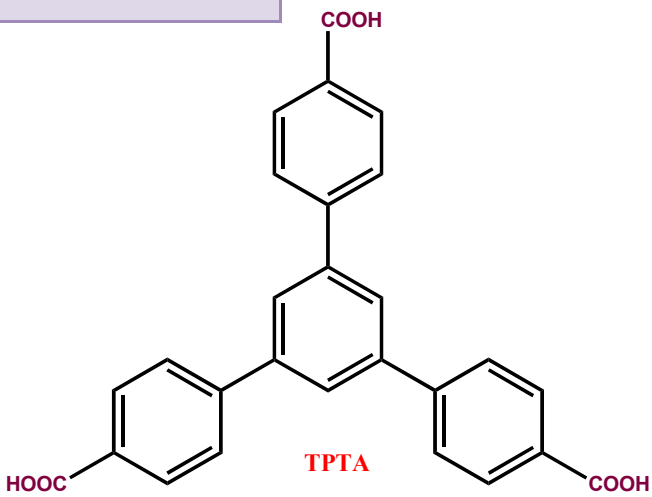
Name	Mol Wt.	Wt. taken (mg)	mmol con.	Mol. Ratio
Aniline	93	94.86	1.02	
TPTA	438.43	113.99	0.26	Acid:aniline=0.25:1
APS	228	232.56	1.02	APS:aniline=1:1
Aniline	93	47.43	0.612	
BPTA	286.24	43.79	0.153	Acid:aniline=0.25:1
APS	228	142.33	0.612	APS:aniline=1:1

COMPOSITE	BPTA PANI	TPTA
YIELD(mg)	37.9	52.64



BPTA

Biphenyl-3,5,4'-tricarboxylic acid



TPTA

1,3,5-tris(4-carboxyphenyl)benzene

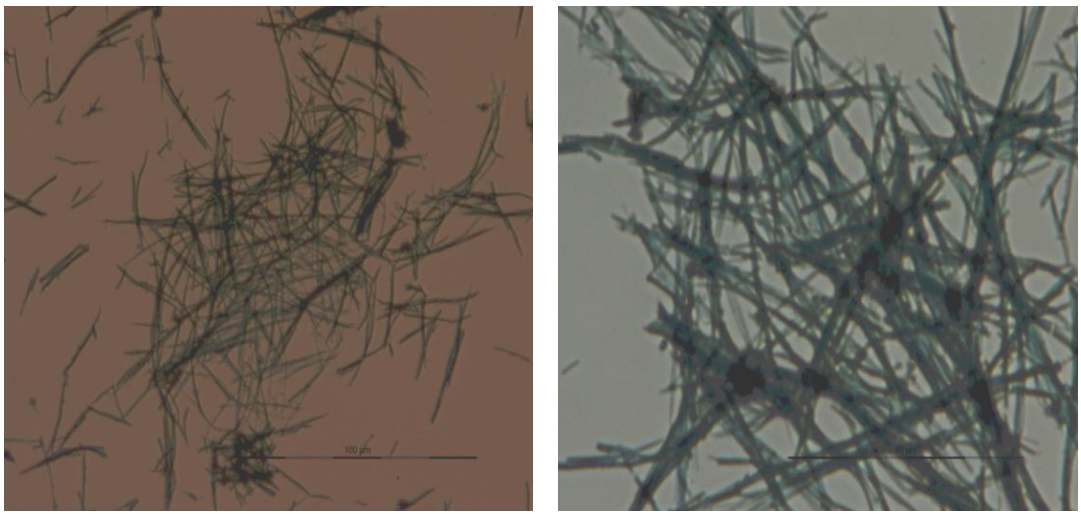


Fig 8: Optical microscopy images of BPTA/BPTA-PANI composite ensure the formation of fibres

FTIR analysis:

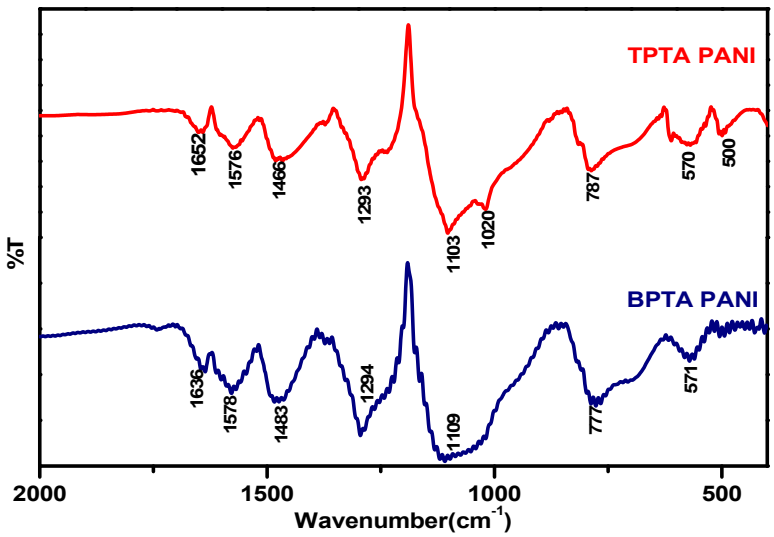


Fig 9: FTIR spectra of TPTA and BPTA PANI /acid composites

Table: 4

Composites	Bands appeared (cm^{-1})					
	C=C quinoid	C=C benzenoid	C-N secondary amine str.	In plane C-H deformation	Doping of PANI with acid	Out of plane C-H deformation
BPTA	1576	1466	1293	1103	1020	787
TPTA	1578	1483	1294	1109	BROAD PEAK	777

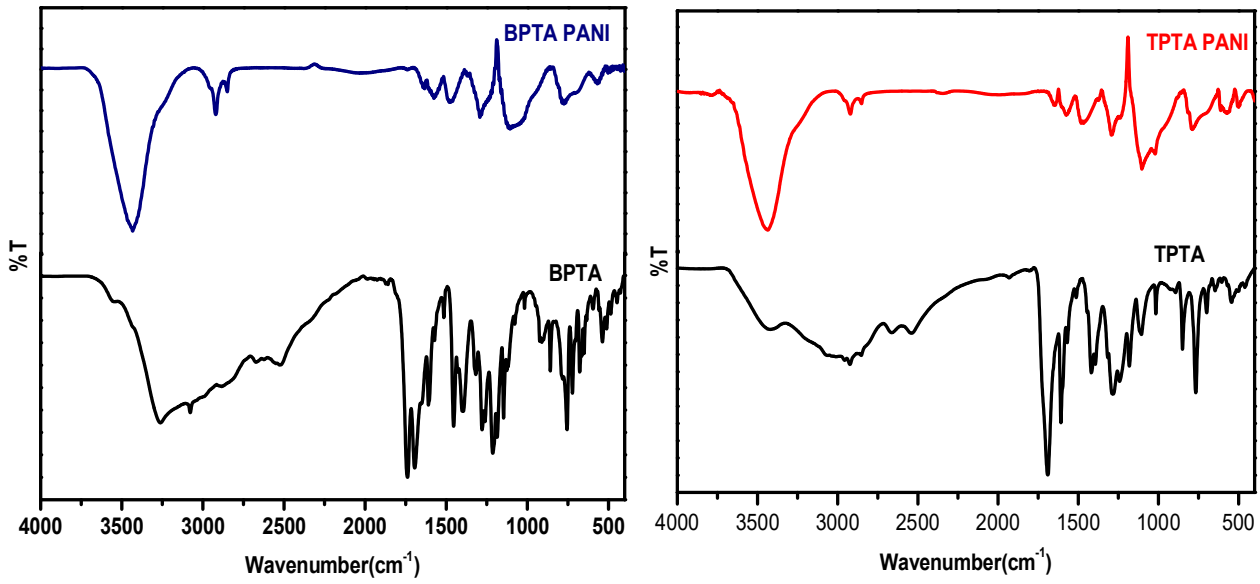


Fig 10: FTIR spectra of PANI-BPTA and TPTA composites with corresponding acids

Characterization by UV-Vis Spectroscopy:

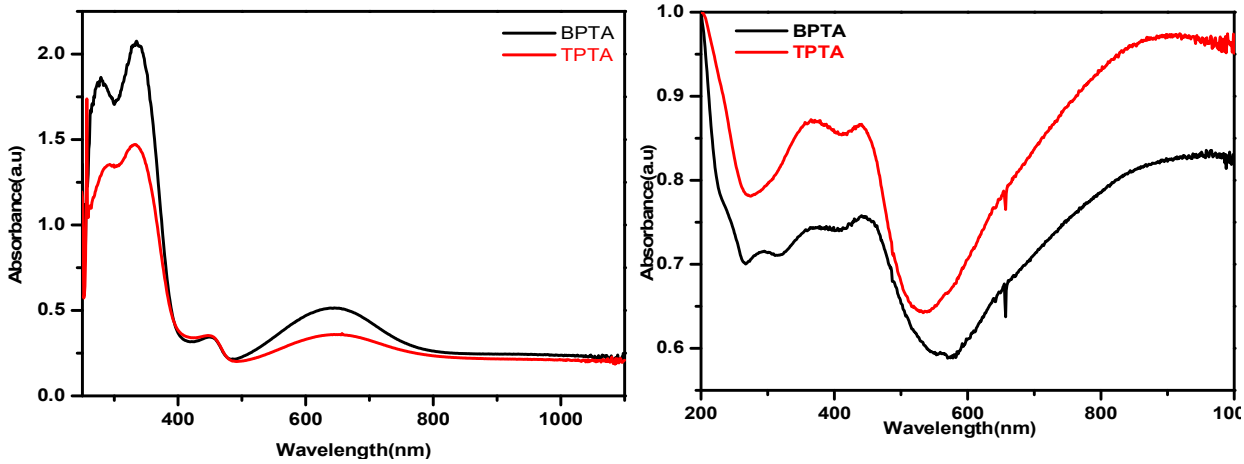


Fig 11: UV-Vis spectra of BPTA PANI and TPTA PANI composites at DMSO and Water(from left to right)

Peaks appeared ~330, ~450 and ~630 nm in DMSO medium and near 365, 450and 900 nm in water. The reasons are discussed earlier.

^{1}H-NMR (500MHz,DMSO-D_6) Spectroscopy:

In the NMR spectra BPTA PANI and TPTA PANI also give three equidistance and equal intense peaks at δ= 6.97, 7.07 and 7.17 ppm.

Effect Of Concentration:

To observe the concentration effect of the dopant acid I have also synthesize PANI with BTA-1 at the [Aniline/Acid] ratio 1:0.10 and 1:0.01 and they are characterized as earlier.

Characterization by UV-Vis. Spectroscopy:

UV-Vis spectroscopy was done by dispersing 0.5 mg of the samples into 2.5 ml water and three peaks centered ~ 360, 450 and 930 nm appeared. The peak at 360 nm is ascribed to the π-π* transition in the benzenoid rings, while remaining two peaks at 450 and 930 nm are attributed to the polaron-π* transition and π-polaron transition, respectively. The increasing intensity of the peak ~450 nm with the increased concentration of BTA indicates that the environment of quinoid and benzenoid rings in PANI chains is apparently changed. The decrease of peak intensity at 930 nm with decreasing the concentration of BTA implies the lesser number of positively charged polarons in PANI chains, i.e., shortening of the conjugation length of PANI chains.

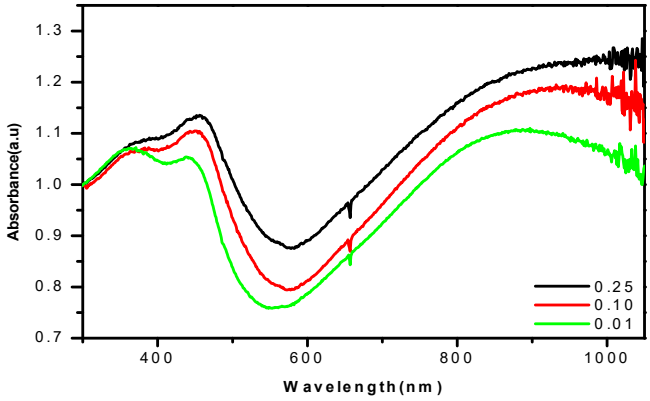


Fig 12: UV-Vis spectra of BTA-1 PANI composites at different acid concentration

Characterization by FTIR spectroscopy:

The ratio of the relative intensities of quinoid to benzenoid ring modes (I_q/I_b) for BTA-1PANI 0.10 and BTA-1 PANI 0.01 are 1.01492 and 1.01392. Thus it reveals that the percentage of imine units are higher than that of amine units in the composites, and the PANI chains are possibly at higher conducting state at higher acid concentration.[8]

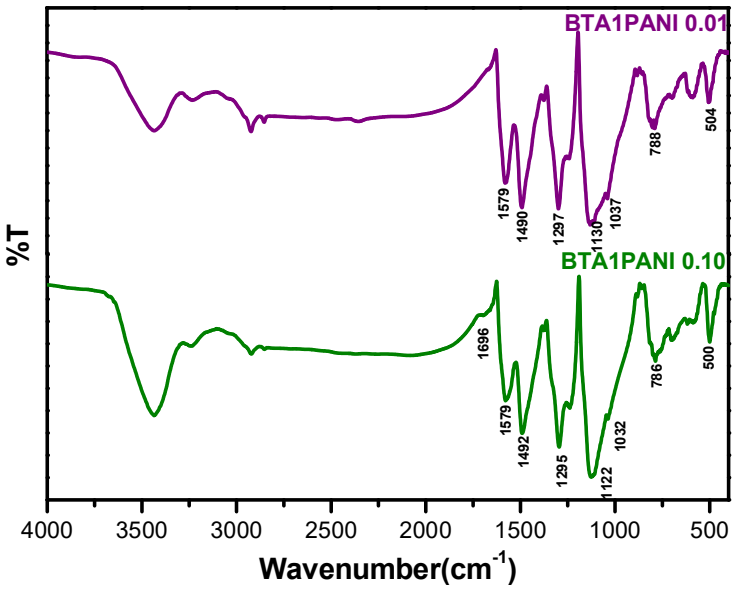


Fig 13: FTIR spectra of BTA-1PANI/acid composites at different concentration

Effect of Solvent:

To study the solvent effect in BTA-1 PANI composite, 0.5 mg of the composite was dissolved in 10 ml of DMSO, DMF, Water, ACN, NMP and THF solvent

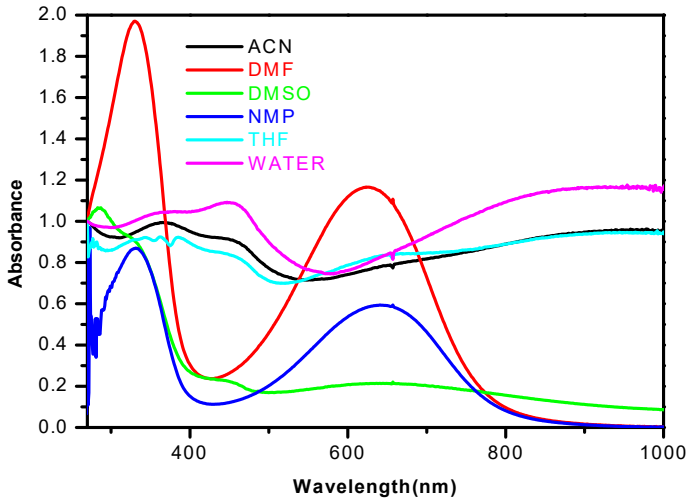


Fig 14: UV-Vis spectra of BTA-1PANI composite at different solvent

It have been observed that for polar aprotic solvents the bands appear at nearly 330 and 630 nm and for polar protic at near 360, 450 and930 nm suggesting that the PANI chain is effected by the proton of the solvent. It is well established that the shift in the electronic transition peak has a relation with the diaelectric constant of the solvent. The spectra show a bathochromic shift of the λ_{max} with the increase in the diaelectric constant of the solvent. It proves that the π_q-π_b transition is highly influenced by the diaelectric constant of the solvent.

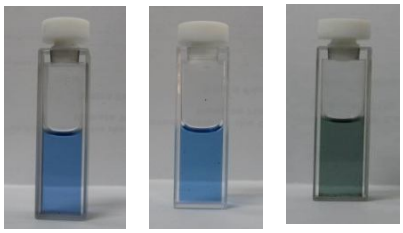


Fig 15: Images of BTA-1 PANI composite solutions in DMF, NMP, DMSO (from left to right)

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