

Effect of Primary Dopants on Morphology & Optical Behavior of Helical Conducting Polyaniline

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Abstract

Various approaches have been established for the preparation of one dimensional nano-structured PANI with controllable morphologies & size. Among all kinds of morphologies (Macromolecular, Micromolecular and Nanomolecular), one dimensional nano-structured PANI exhibits higher surface area, higher conductivity as well as controlled chemical/ physical properties & good environmental stability. This renders the nanomaterials promising candidate for application ranging from sensors, energy storage and flash welding to digital non-volatile memory. Although, a number of chemical oxidative approaches had been reported for the synthesis of helical conducting polyaniline through simple in-situ oxidative doping of non-conducting polyaniline, yet the effect of different acidic dopants on chiral dopants has not been reported. This study attempts to address the effect of primary dopants on the helicity and conductivity of the helical conducting polymer. PANI was doped using various dopant acids, undoped and re-doped by optically active dopants. The characterization of helical conducting polyaniline was done by using UV and FTIR Spectroscopy. The helicity was observed by Circular dichorism (CD) Spectra. Conductivity measurement was done by four probe assembly and surface morphology was studied by SEM.

1. Introduction

Discovery of polymers has given a new dimension to the present era. Polymers are known so far as a class of heat sensitive, flexible, electrically insulating amorphous

materials. Polymers are generally known for their insulating properties because of the presence of covalent bonds in saturated carbon compounds. Since desired properties can be conveniently attained by tailoring the polymer structure and also by incorporating additives; scientists have been enthusiastic to explore the possibility of transforming insulating polymers into conducting or semiconducting materials envisaging such a special characteristics like low density, ease of fabrication, flexibility of design, low energy & labour requirements for fabrication and processing.

Present investigation deals firstly with the synthesis of polyaniline by oxidative chemical polymerization using different acidic dopants like HCl, p-TSA (para toluene sulphonic acid) and Acetic acid and then redoping with optically active dopant, (+) and (-) Tartaric Acid. The effect of redoping on morphology, conductivity and helicity have been presented soluble in the same solvents. PANI was produced by simple chemical polymerisation with hydrochloric acid (HCl), p-TSA (para toluene sulphonic acid), DBSA (Dodecyl benzene sulphonic acid) and Acetic acid as dopants. Samples with PANI concentration of 15% was taken for characterization of helical conducting polyaniline was done by using UV and FTIR Spectroscopy. The helicity was observed by Circular dichorism (CD) Spectra. Conductivity measurement was done by four probe assembly and surface morphology was studied by SEM.

2. Experimental

2.1 Materials

Aniline, Ammonium per sulphate (APS), p-Toluene sulphonic acid (p-TSA), Xylene and Methanol were supplied by Loba Chemie India, while Hydrochloric Acid (HCl) and Acetic Acid, Ammonia solution were purchased from Qulaigens India, and (+) Tartaric acid, (-) Tartaric acid were purchased from CDH Laboratory were used as received.

2.1 Synthesis of Conducting Polymer

Chemical synthesis of conducting polymers involves the oxidation of the monomer, viz aniline with the oxidizing agents such as APS in different acidic medium (HCl, p-TSA, and Acetic acid subsequently) to initiate the polymerization. Solvent used for the solution polymerization was deionized water.

Synthesis of polyaniline involved single step oxidative polymerization, in which the polymerization and doping occurs concurrently. For the synthesis of polyaniline freshly double distilled Aniline 0.2 M (1.86 gm), was dissolved in 100 ml of 1M HCl Solution to make aniline solution (colourless) and 0.2 M (4.56gm) APS was dissolved in 100 ml of deionized water to form APS solution (colourless). Both the solutions i.e., aniline solution and APS solution were kept at low temperature about 1°C to decrease the rate of reaction as the oxidation of polyaniline by APS is an exothermic reaction. APS solution was poured over the aniline solution drop by drop while aniline solution was kept under stirring. As the polymerization reaction starts, the colourless mixture begins to turn blue and as the reaction progresses further the solution turns into dark green precipitate which is the symbol of completion of polymerization. The solution was kept on stirring for about 3 hrs. After 3 hrs the solution was filtered, the dark green paste so formed was washed firstly with deionized water and then with methanol till the filtrate becomes colourless and then dried at room temperature.

Same procedure was followed for other dopants while concentrations were varied. In case of p-TSA doped PANI, 0.6 M (11.40 gm) p-TSA was dissolved in 600 ml of deionized water and 0.6 M (5.58 gm)

Aniline was dissolved in this acidic solution (p-TSA). 0.6 M (13.86 gm) APS was dissolved in 50 ml of deionized water and poured into aniline and p-TSA mixture drop by drop. For the synthesis of acetic acid doped polyaniline, 0.2 M (1.86 gm) Aniline was dissolved in 50 ml of 0.4 M Acetic acid and equimolar APS solution was added.

2.2 Dedoping of Polyaniline Emeraldine Salt

To convert conducting polyaniline emeraldine salt into nonconducting emeraldine base dedoping is done. For dedoping prepared polyaniline salt was stirred with 30% ammonia solution for about 1 hr and kept for about 24 hrs, then filtered, washed with deionized water and methanol till the filtrate turns into colourless and then dried in oven at 60 °C for about 3 hrs, the filtrate obtained was in brownish colour. This brownish filtrate was nonconducting emeraldine base.

2.3 Redoping of Polyaniline Emeraldine base with Optically active Dopant

Nonconducting emeraldine base was redoped with optically active dopant (+) tartaric acid and (-) tartaric acid to form helical conducting polyaniline. For redoping, few grams of emeraldine base were stirred with aqueous solution of tartaric acid prepared in equimolar ratio to the emeraldine base. The solution was stirred for 24 hrs at room temperature. After 24 hrs the solution was filtered, washed with deionized water and methanol till the filtrate turns colourless, and then dried in oven at 60 °C for about 3 hrs. The re-doped PANI thus obtained was dark green fine powder.

$$W_{TA} = W_{EB} \times M_{wTA} \div M_{wAni} \times 2$$

Where, W_{TA} = Weight of Tartaric acid

W_{EB} = Weight of Emeraldine base

M_{wTA} = Molecular weight of Tartaric Acid

M_{wAni} = Molecular weight of Aniline

3. Characterization

The conductivity measurements were carried out by a four-point probe technique recorded by a (Keithley 220 Programmable Current Source and 181 Nanovoltmeter). Scanning electron micrographs (SEM) were obtained with a ZEISS EVO series scanning electron microscope model EVO50 at an acceleration voltage of 10 kV. IR spectra of the samples was taken using a spectrometer (Perkin Elmer).

4. Results & Discussions

4.1 Conductivity Measurement

Electrical DC- Conductivity of PANI (doped with different acids), was measured using conventional 4-point probe technique. In order to measure conductivity, the polymeric samples were turned into small pellets of 2×4 mm size. Conductivity measurement reveals that transfer of charge in the polyaniline formed after secondary doping varies with different primary doping agents. This may be attributed to the reorientation of the PANI chain structure and redistribution of hopping sites within the chains. PANI synthesised with HCl as dopant showed maximum conductivity, but after de-doping and re-doping the conductivity decreases. This may be due to changes in orientation of charge conveying sites during de doping. While p-TSA doped PANI retains its conductivity characteristics after redoping. Presence of huge TSA groups induces permanent orientation of charge transfer sites along the PANI backbone. It was also observed that Optical variants of the same doping acids also show difference in conductivity. This may be due to variation in location of hopping sites along the back bone corresponding to the direction of optical activity.

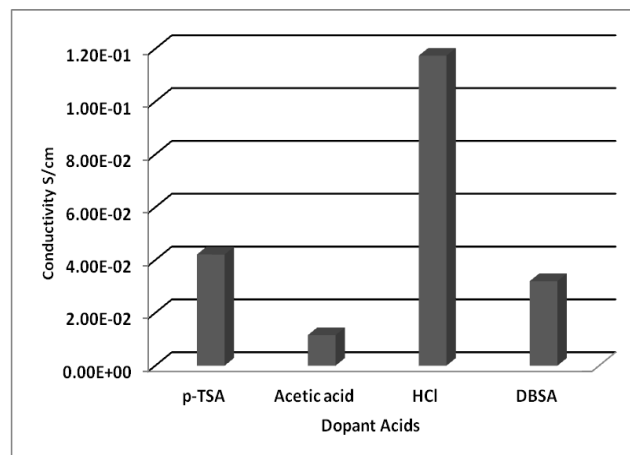


Figure 1. Conductivity of PANI Doped with different Acids

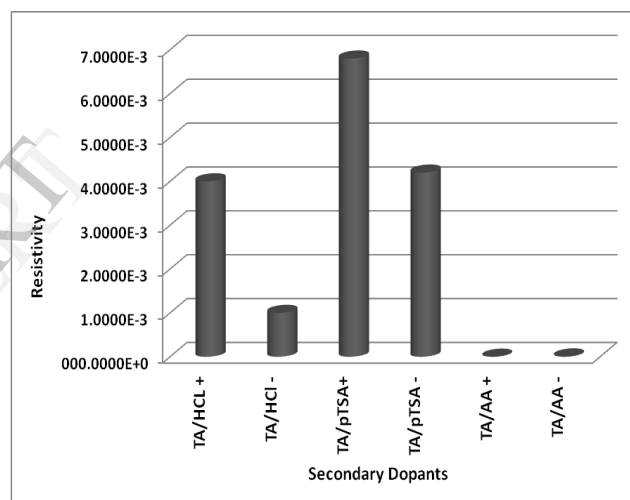


Figure 2. Conductivity of PANI after Redoping with Tartaric Acid

4.2 Morphological Studies

Morphological studies of PANI doped with different acids were done using Scanning Electron microscopy. SEM micrographs reveal that there is no significant variation in the morphology of samples with different primary Dopants. A tubular structure is seen but it could not confirm the presence of helix. It may be inferred that primary Dopants may have a significant effect on morphology but there is no prominent difference evident after redoping with optically active Dopants. The exact change in PANI

back bone was not visible under SEM. It has been reported that HCl doped PANI shows large agglomerates but after redoping with \pm Tartaric acid there is no evidence of agglomeration.

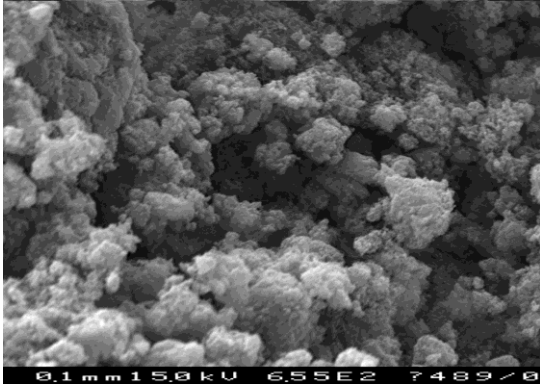


Figure 3. + Tartaric acid doped p-TSA PANI

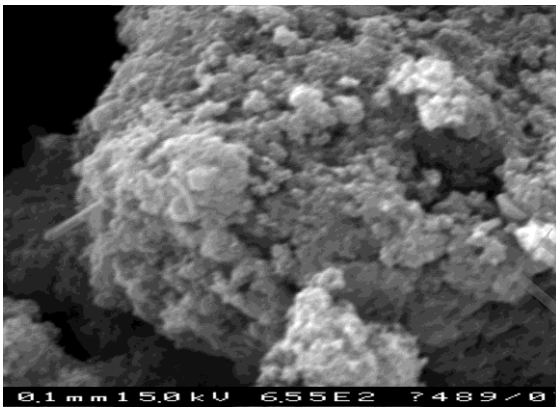


Figure 4. Acetic acid doped PANI

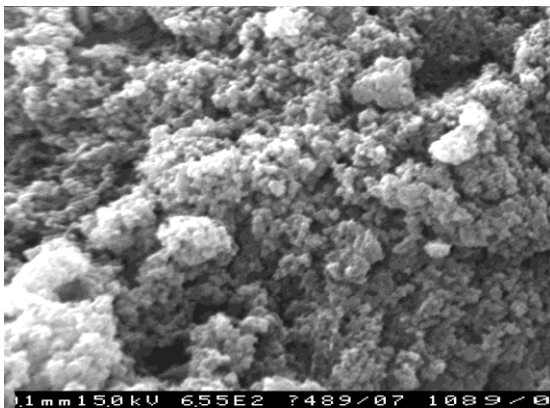


Figure 5. HCl doped PANI

4.3 Circular Dichorism

Helical conducting polyaniline was synthesized by using optically active dopants. Circular dichorism was used to study the optical activity. It is clear from the data a separate absorption peaks have been observed in (+) tartaric acid and (-) tartaric acid. Primary dopants have a visible effect on helicity. In case of HCl doped PANI redoping with (+) and (-) tartaric do not show much variation. This may be attributed to strong doping nature of HCl by virtue of which it imparts a permanent change in PANI back bone which is unaffected by the chiral behavior of secondary dopant. But in case of p-TSA doped PANI shifting of peak near about 450 nm can be observed, sharp helical peaks are found at around 400 nm on redoping with (+) tartaric acid. This difference is because p-TSA has higher ionic radii as hence causes variable deformation to the PANI back bone on doping. In case of acetic acid no profound peak could be observed. The peak shifts towards higher value. Acetic acid at this concentration tends to form tubular structure and hence could not produce a marginal change to the conducting backbone of PANI chains. Thus the effect of secondary dopant was reasonably less.

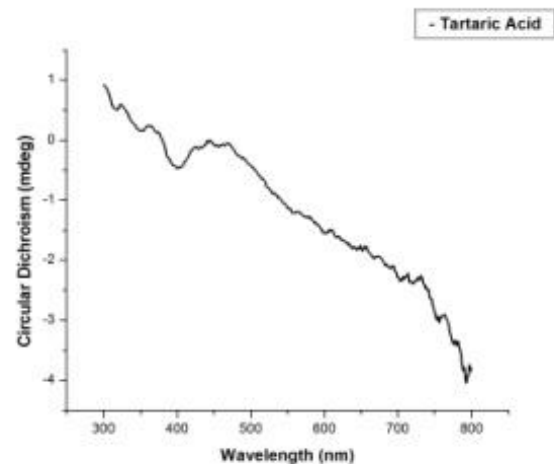


Figure 6. CD Graph of (-) Tartaric Acid

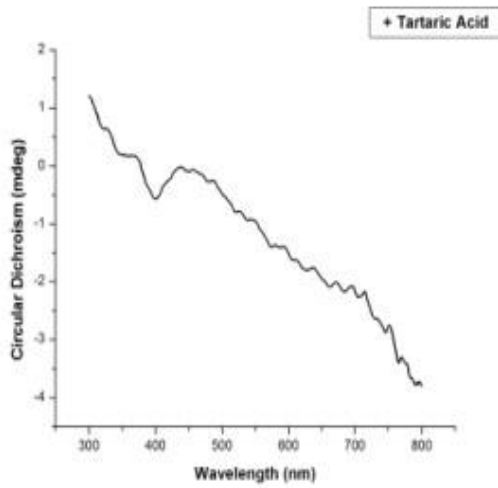


Figure 7. CD Graph of (+) Tartaric Acid

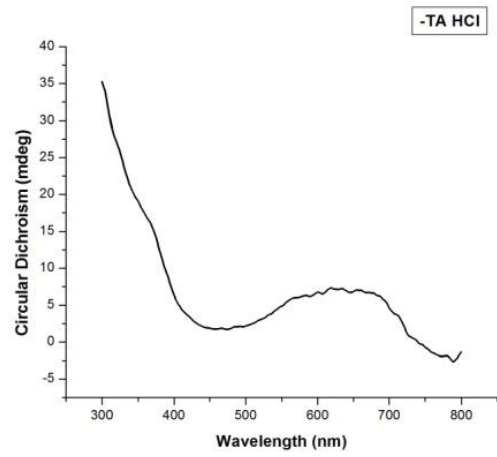


Figure 9. CD Graph of (-) Tartaric Acid Doped HCl/PANI

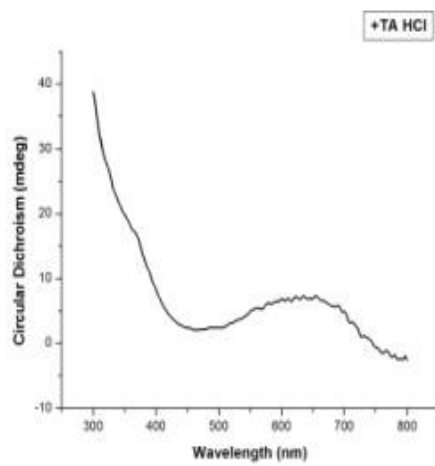


Figure 8. CD Graph of (+) Tartaric Acid Doped HCl/PANI

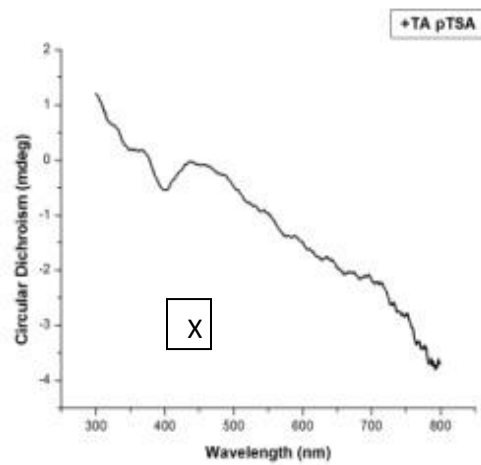


Figure 10. CD Graph of (+) Tartaric Acid Doped p-TSA/PANI

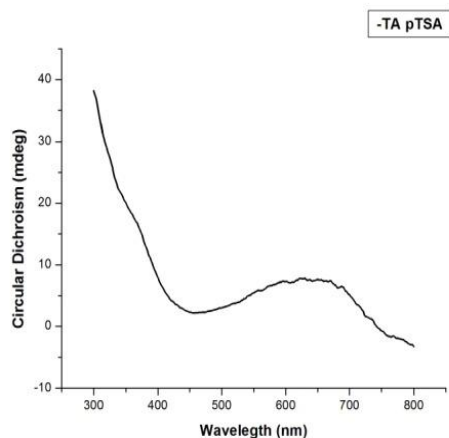


Figure 11. CD Graph of (-) Tartaric Acid Doped p-TSA/PANI

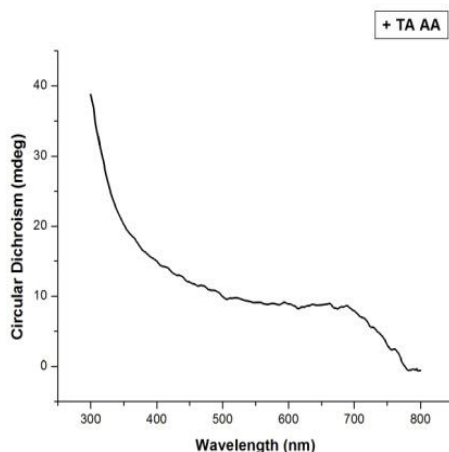


Figure 12. CD Graph of (+) Tartaric Acid Doped Acetic Acid /PANI

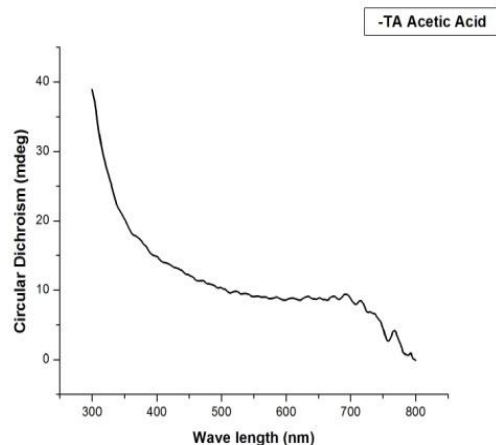


Figure 13. CD Graph of (-) Tartaric Acid Doped Acetic Acid/PANI

4.4 FTIR measurement

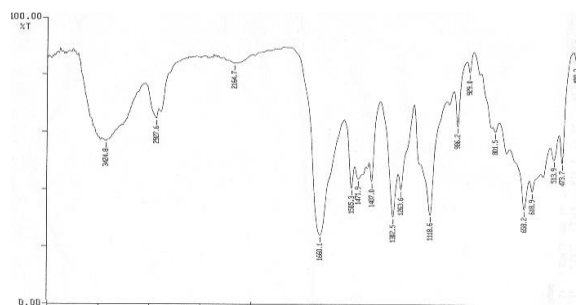


Figure 14. FTIR of HCl doped Polyaniline

IR spectra of the samples shows about eight principal absorption peaks at 3436, 2925, 2359, 1567, 1487, 1300, 1124, & 817 cm^{-1} . The peaks at 3436 cm^{-1} corresponds to $-\text{NH}_2$ stretching, peak observed at 2925 cm^{-1} is attributed to C-H stretching & C-N stretching is observed at 1300 cm^{-1} . The peaks at about 1124 cm^{-1} are attributed to C-C stretching. The band at 1567 & 1487 cm^{-1} are attributed to C=N & C=C stretching modes of vibration for the quinonoid & benzenoid units, respectively. The observation obtained by the IR spectra of polyaniline doped with different acids shows slight variations in their specific pecks at 3436 cm^{-1} (for $-\text{NH}_2$ - stretching), 1567 cm^{-1} (for $-\text{C}=\text{N}$ - stretching) & 1487 cm^{-1} (for $-\text{N}=\text{N}$ -) stretching's.

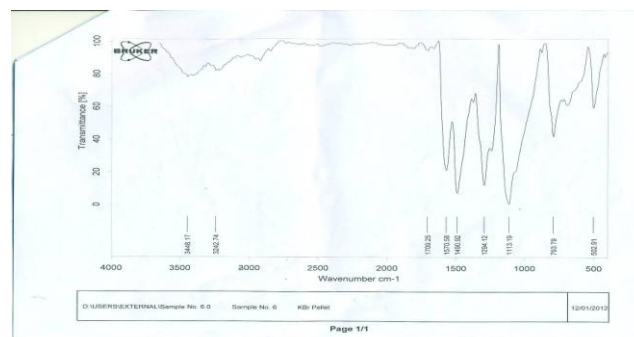


Figure 15. FTIR of + Tartaric Acid Doped HCl/PANI

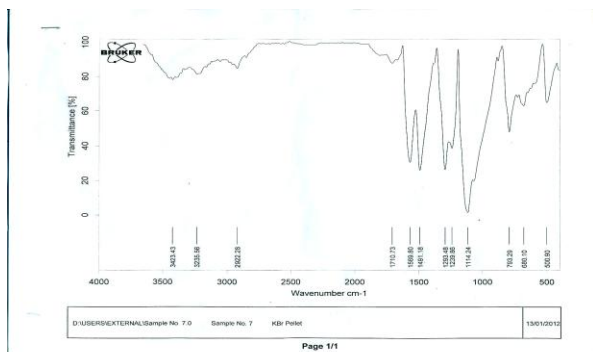


Figure 16. FTIR of - Tartaric Acid Doped HCl/PANI

In case of HCl doped polyaniline the $-NH_2$ -stretching peaks at 3436 cm^{-1} shifts to 3420 cm^{-1} & its redoped samples shifts to 3448 cm^{-1} & 3423 cm^{-1} on redoping with +Tartaric acid & -Tartaric acid respectively. While the $C=N$ stretching peaks shifts from 1572 to 1570 & 1569 cm^{-1} , $C=C$ stretching peaks from 1470 cm^{-1} to 1490 & 1491 cm^{-1} after redoping with +Tartaric acid & -tartaric acid respectively. This shifts of peaks are the results of helicity developed into the polyaniline chain because of the redoping with optically active dopants.

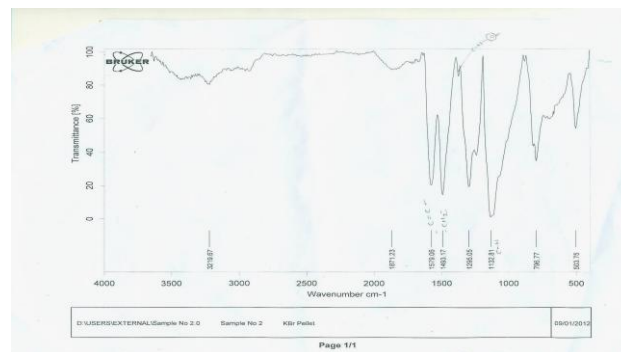


Figure 18 FTIR of - Tartaric Acid doped p-TSA/PANI

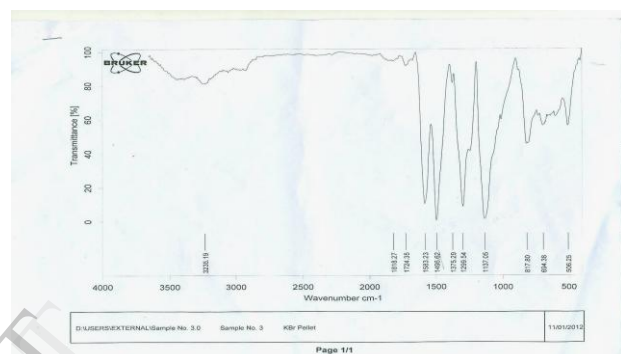


Figure 19 FTIR of + Tartaric Acid doped p-TSA/PANI

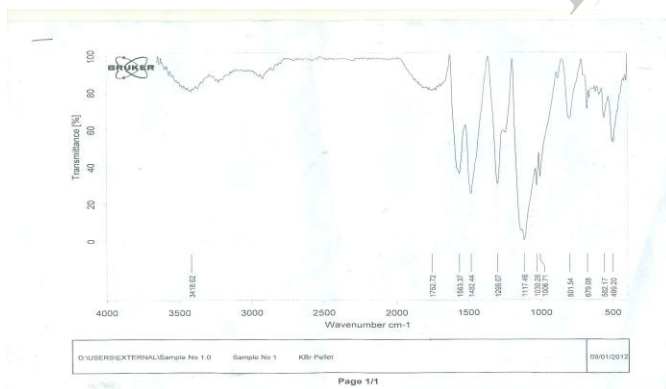


Figure 17 FTIR of p-TSA doped Polyaniline

In case of Acetic acid doped polyaniline the $-NH_2$ -peak do not show so much variation on redoping, but $-C=N-$ & $-C=C-$ stretching peak shows a large shifting. $-C=N-$ stretching peak shifts from 1566 cm^{-1} to 1500 cm^{-1} & $-C=C-$ stretching peak shifts from 1483 cm^{-1} to 1444 cm^{-1} . The specific IR absorption peaks at 3228 cm^{-1} in acetic acid doped polyaniline confirms the formation of some tubular structure.

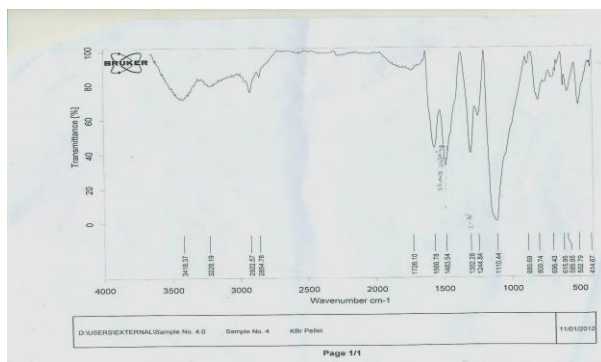


Figure 20. FTIR of Acetic Acid doped Polyaniline

On Redoping, basic chemical structure & orientation remain same. But stretching along C=N, & NH₂ is increased. This may be due to the change in alignment of side chains. Helicity may induce changes in orientation of side groups around the C=C backbone but the basic structure of polyaniline remain unchanged.

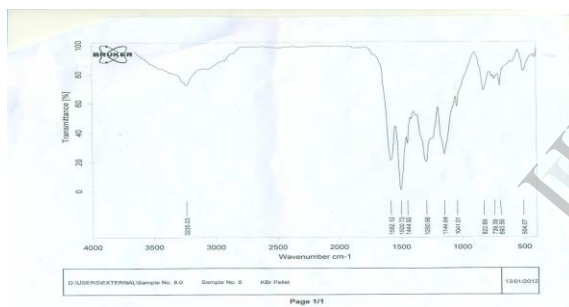


Figure 21 FTIR of - Tartaric Acid doped Acetic Acid/PANI

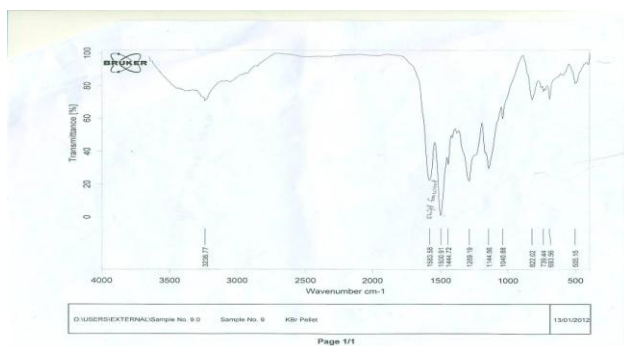


Figure 22. FTIR of + Tartaric Acid doped Acetic Acid/PANI

5. Conclusion

Although, the chiral properties are induced by the secondary optically active dopant, yet primary dopants also have a remarkable effect on helicity and conductivity. From the present work it can be inferred that

FTIR shows that there is a varied change in the C=C stretching after redoping with optically active dopants. The level of structural reorientation depends on the characteristic change brought about by primary dopants in the polyaniline backbone. Hence the corresponding stretching results at C=C backbone.

Conductivity measurement reveals that transfer of charge in the polyaniline formed after secondary doping varies with different primary doping agents.

This may be attributed to the reorientation of the PANI chain structure and redistribution of hopping sites within the chains. Optical variants of the same doping acids also show difference in conductivity. The presence of optically active dopant may cause the hopping sites to vary and thus conductivity varies. CD spectra of polyaniline doped with different primary Dopants, varies indicating that the structural orientation induced by primary dopant remains intact even after dedoping. Acetic acid doped polyaniline is reported to form a complex tubular structure hence, redoping of the same failed to produce any optical activity.

SEM micrographs do not show any prominent morphological difference in polyaniline samples even after redoping by (\pm) Tartaric acid. Although formation of tube like structures is evident, yet the specific identity could not be confirmed.

This study paves the way for further research in this direction to identify the root cause behind the

variation in structural re-orientation of Polyaniline doped with different Dopants. Exact morphological variation may be studied by using TEM etc.

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