



Structural, Optical and Electrical Characterization of Camphor Sulfonic Acid Doped Poly (2, 5-Dimethoxyaniline) Thin Film

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Abstract

Emeraldine Base Poly (2, 5-dimethoxyaniline) has been synthesized by oxidative polymerization using ammonium per sulfate as an oxidant. Protonated Poly (2, 5 - dimethoxyaniline) have been achieved by doping with Camphor sulfonic acid with different weight ratio as 1: x (x=0, 0.25, 0.5, and 1). Poly (2, 5-dimethoxyaniline) Emeraldine Salt was spin coated as thin film by using m-cresol solvent cum secondary dopant. Camphor sulfonic acid doped Poly (2, 5-dimethoxy aniline) thin films were characterized by UV-V spectrophotometer, Fourier Transform Infrared spectroscopy, X-RAY Diffraction, PL for the analysis of band gap, chemical composition, structural confirmation and electronic transition. SEM micrograph images exposed the changes of plate structure to rod for Poly (2, 5-dimethoxyaniline) thin films. The band gap of pristine Poly (2, 5-dimethoxyaniline) thin film was found as 3.67eV. The level of dopant was found to influence the band gap and the DC conductivity of Camphor sulfonic acid doped Poly (2, 5-dimethoxyaniline) thin films.

Key words: Camphor sulfonic acid, m-cresol, Poly (2, 5-dimethoxy aniline), protonation, thin film.

Introduction

The p-type and n-type states are the specific molecular structure of the conjugated polymers due to doping. The main chain of the conducting polymer gets oxidized to 'p' type phase by the acidic dopant [1]. The acid doped conducting polymer is composed of holes due to oxidation leading to a p type conjugated polymer. This type shows about the molecular structure by conducting, polymers need significant consideration due to their exceptional tunable electrical and optical, mechanical and thermal properties with variation in dopant level [2]. Fundamentally conducting polymers are conjugated molecular structure that place π electrons delocalized through entire polymer chain. These 'p' type polymer are in the form of Photo voltaic cells [3], Field effect transistors [4], Gas sensors [5], Biosensors [6] and Micro-Electro-Mechanical System (MEMS) devices [7], Organic light emitting diodes (OLEDS) [8]

While conducting polymers, Poly (p-phenylene vinylene) (PPV), Polypyrrole (PPY), Polyaniline (PANI), Poly (3, 4-ethylenedioxythiophene) (PEDOT), Polythiophene (PT) and Polyacetylene (PA) are the exceptional polymers. Some literature of the p- type conducting polymers are discussed about the counter of electrode in dye sensitized solar cells [9], as hole transport layer in perovskite solar cells [10], electron acceptor with fullerene or n-type semiconductor forming a photoactive or heterojunction layer respectively[11].



The member of conducting polymers is Polyaniline (PANI) with high electrical conductivity, good optical properties, environmental stability and ease of synthesis. PANI based hybrid films are preferred as remarkable capacitor electrodes, corrosion protecting layer, active material for energy storage device, photo catalyst, gas sensors, anode for DSSC and as well as lithium ion batteries in recent times [12].

Undoped Polyaniline (PANI) will exist in three phases through insulating nature namely, (a) Fully reduced Leucoemeraldine, (b) half oxidized Emeraldine Base and (c) fully oxidized perigraniline [13]. Emeraldine Base of PANI possibly doped in organic and inorganic acid which is protonated resulting in the hole generation (positive charge carriers) along with the entire main chain of the PANI [14]. Poly (2, 5-dimethoxyaniline) (PDMA) is a substitute derivatives of PANI with methoxy groups ($-OCH_3$) were substituted in ortho and meta-positions [15]. The methoxy group has higher electron donating property in the form of unshared electron pair to the connected phenyl rings [16]. Poly (2, 5-dimethoxyaniline) has enormous potential applications as Electro Chromic Device which is excellent in its properties [17]. PDMA acts as Schottky diode with polyethylene oxide blend [18], Immuno sensor [19], Humidity sensor with WO_3 (tungsten oxide) composite[20], Electrodes[21], Electrochemical capacitor [22] and Glucose biosensor [23].

The DC conductivity values of PDMA in different configuration ranges in the order of 10-9 to 10-2S/cm[24]·[25]·[26]·[27]· [28]·[29]. Potential combination of m-cresol solvent and camphor sulfonic acid as dopant for Polyaniline make its conductivity higher in the adaptation of coil like conformation of PANI molecules to linear crystalline structure [30]. The objective of the present study is to make an attempt to dope PDMA with Camphor sulfonic acid (CSA) and m-cresol solvent to obtain p type material through the steps as follows;

- In this connection PDMA has been synthesized by oxidative polymerization method and it is doped with CSA and m-cresol solvent to obtain p-type materials.
- The structural confirmation has been carried out through XRD and SEM analysis.
- The conducting nature of the material is probed through PL analysis and the band gap of the material was taken from UV-V absorption spectrum.
- The functional group has been identified through FTIR analysis.
- The thickness of the film is estimated by gravimetric method.
- Room temperature DC conductivity of the material is calculated from IV characteristics.

Experimental

Synthesis of Poly (2, 5-dimethoxyaniline)

Poly (2, 5-dimethoxyaniline) have been synthesized by oxidative polymerization through monomer and Ammonium peroxodisulfate (APS) as 1:1 molar ratio of DMA oxidant. DMA dissolved in 1M HCl and stirred at a temperature of 0 to 5°C for thirty minutes. For this pre-cooled solution an aqueous solution of APS in 1 M HCl is added in the form of drop by drop until brown color monomer turns into green color solution of HCl doped Emeraldine Salt (ES) indicating the formation of polymer, PDMA. The solution was stirred for another 5 hours, then filtered using Whitman paper and washed with deionized water to remove the unreacted monomers. The



filtered ES - PDMA was dried in open hot air condition for 2 hours. Emeraldine Base (EB) had been prepared by leaving a part of ES-PDMA in 1M NH_4OH solution. The solution was stirred for 3 hours, filtered and washed with diethyl ether to obtain EB form of PDMA. It was dried in open hot air condition for an hour to get deep blue color powder form of EB- PDMA. EB - PDMA is mixed with Camphor sulfonic acid in diverse weight ratios 1: x ($x = 0.25, 0.5$) using pestle mortar to obtain the protonated green color ES-PDMA. For the mixer ratio 1:1, the final product was obtained to be blue color which is the fully oxidized state of the polymer.

Preparation of ES - PDMA thin film:

The protonated ES-PDMA obtained in different weight ratio were dissolved in 2ml of m-cresol solvent with constant stirring for 30 mins. The viscous solution was spin coated under 1500 rpm for 60 seconds to get thin film over precleaned fluorine doped tin oxide coated glass substrate and as well as on glass substrate. The thin films were dried under open air condition over a hot plate maintained at 60°C for 5 hours. The films were designated as CP1, CP2, CP3, and CP4 analogous to weight ratio 1:0, 1:0.25, 1:0.5, 1:1 respectively.

Material characterization

X-ray diffraction of the thin films was performed using XPERT-PRO Diffractometer with $\text{Cu K}\alpha_2$ radiation. Scanning electron microscopic (SEM) of PDMA thin films were observed using ZEISS EVO 18. Fourier transform infrared (FTIR) spectra of the thin films were obtained by Perkin Elmer spectrum Rx1 spectrometer. UV-Vis spectra of the thin films were obtained using Lambda 365 Perkin Elmer spectrophotometer. DC conductivity by two probe method for thin films were carried out by Keithley source meter model 2450. The thickness of the films were measured using Gravimetric method.

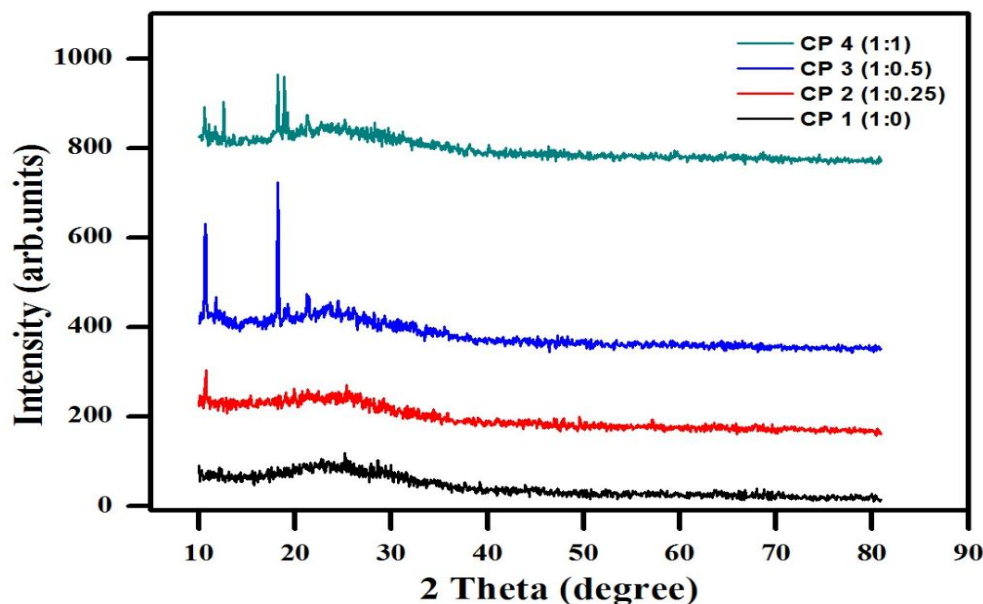
Results and discussion

X-ray diffraction

The x - ray diffraction pattern of pristine (CP1) and doped ES- PDMA (CP2, CP3, CP4) thin film are shown in the Figure1. The absence of sharp peaks in the x-ray spectrum of CP1 reveals the amorphous nature of EB PDMA. The characteristic of crystalline CSA confirms the doped condition of PDMA film at 20.6° and it can be observed in CP3 and CP4 [31]. The peaks at 10.7° , 23.6° and 27° are observed for all doped samples indicating prorogated and crystalline ES-PDMA. The small peaks around $2\theta = 20.6^\circ$, 25° and 27° are due to the periodicity parallel and perpendicular to the polymer chain which appeared as the dopant level was increased confirming the ordered molecular arrangement of PDMA[32] ' [33]. The crystallite size was calculated for sample CP3 using Scherrer equation and found to be 85nm. The crystalline nature of PDMA depends upon the dopant level of CSA that may be due to the elongated chains of the doped polymer and the influence of the secondary dopant m-cresol to form the bridge between CSA and PDMA [34]. CSA with m-cresol solvent constant disturbs the linear arrangement of the main chain may be due to direct bonding between CSA and PDMA.



Fig. 1 XRD pattern of Pristine and CSA doped PDMA thin films

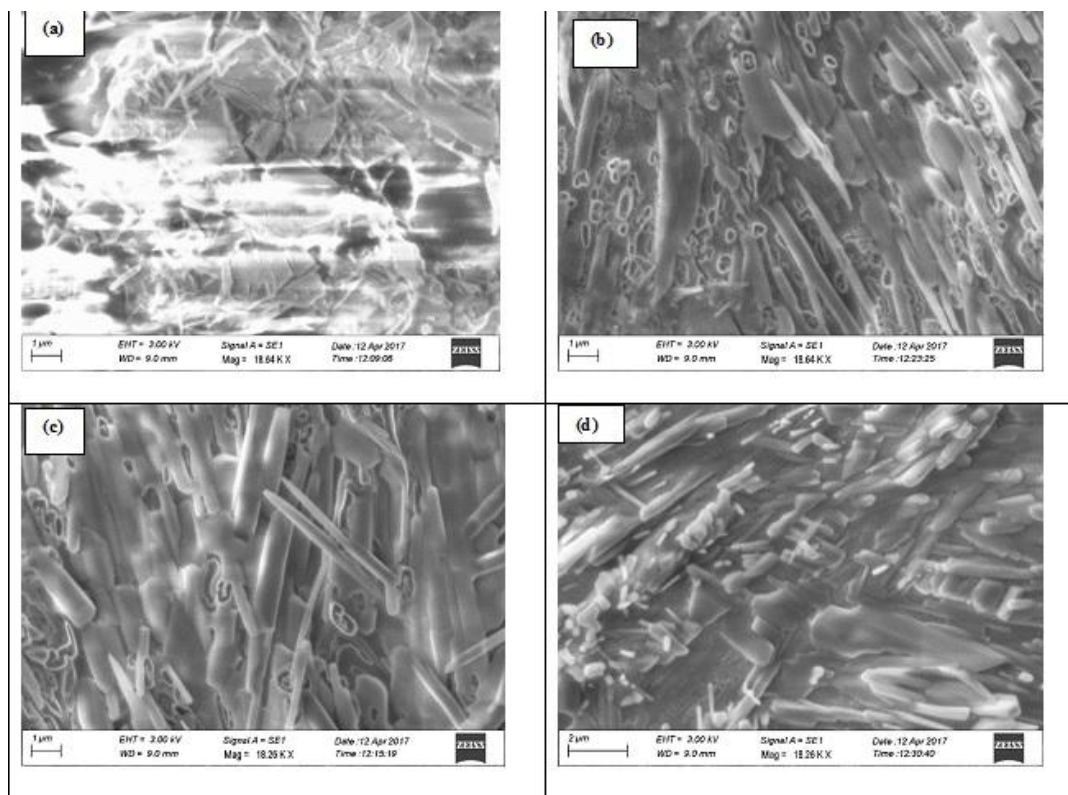


3.2 Surface morphology

The SEM images of the pristine and CSA doped PDMA thin films are shown in Figure 2 (A) and 2 (B), (C), (D) respectively. The SEM images illustrate the morphological changes from plate structure to rod with the increase of the dopant concentration. On doping with CSA the main chain of the polymer stretches due to CSA - PDMA and also CSA- m-cresol-PDMA bond. The CSA- PDMA bond is due to the association of H^+ with Nitrogen of PDMA and the second bond is formed due to π - π stacking interaction of m-cresol with PDMA [35]. Due to the linearization of main chain the rod like structure is experimental representing the crystalline nature of the material figure 2(b) and (c). Beyond the limiting concentration of the dopant material become less crystalline may due to the predominant CSA-PDMA bonding disturbing the linear structure figure 2(d).



Fig. 2 SEM images of Pristine and CSA doped PDMA thin films



Optical properties of pristine and doped PDMA

The optical absorption spectrum of the pristine and CSA doped PDMA thin films wavelength decrease from 200nm to 1100nm which is given in Figure 3. The absorption peaks (not given) for the films show peaks between 305 nm to 330 nm which is due to π - π^* transition of the Benzenoid rings. The existence of EB in pristine PDMA thin film was confirmed by the peak at 592nm and the thin film CP3 exhibits broad peak between 450 nm and 500 nm which conjugated into double bonds of prolongation and the broad peak around 850 nm corresponds to formation of ES -PDMA. The change of state of the polaron from confined to a small area to large state was confirmed by the red shift and the absorption peak around 850 nm corresponds to complete polaron delocalization indicating the structural change of PDMA from compacted coil form to stretched coil like structure.[36] The CP4 thin film shows a peak at 307 nm representing the Emeraldine base of blue color due to direct bonding between CSA and PDMA with concentration of CSA. It also shows decrease in intensity of absorption due to steric repulsion of -OCH₃ group leading to decrement of conjugation length in PDMA [27].

To determine the optical band gap, the fundamental law,

$$\alpha = A (E_g - hv)^n$$

where α is the absorption coefficient, hv is the photon energy in eV, A is a proportionality constant, $n = \frac{1}{2}$ for direct transition and $n = 2$ for indirect transition. Plotting $(\alpha hv)^n$ versus hv for N values to get a linear graph from which the optical band gap of the material was noted from the extrapolation of the linear portion of the graph shown in Figure 4. The optical band gap of

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pristine and CSA doped PDMA for different dopant level were determined as 3.67eV 2.55 eV, 2.21 eV, and 3.56 eV. The group gap value found to be decreased in comparison with the value of CSA doped PANI semiconductor nanofilms reported by Geethalakshmi et al. (2015)

Fig. 3 UV-Vis Absorption spectrum of Pristine and CSA doped PDMA thin films

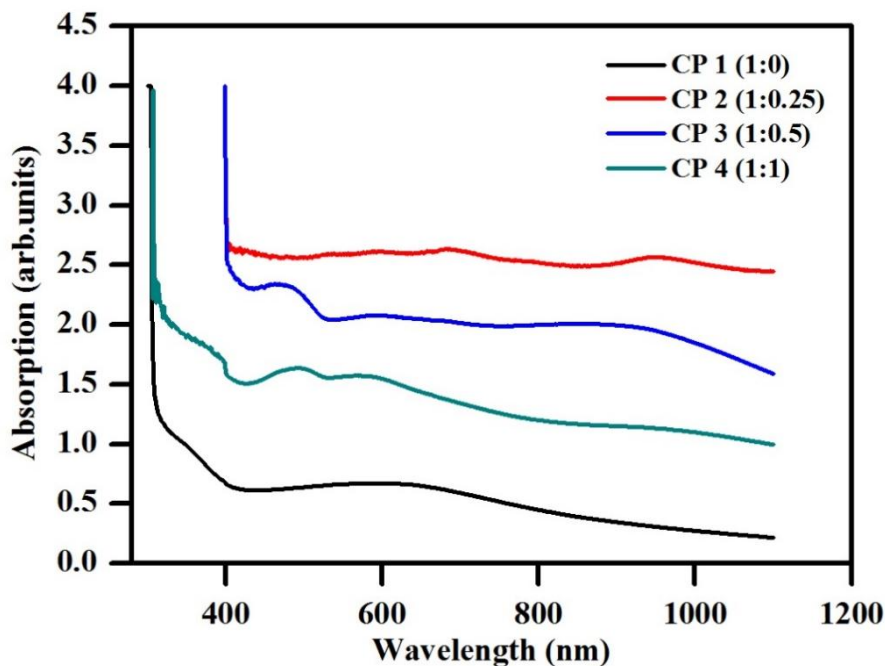
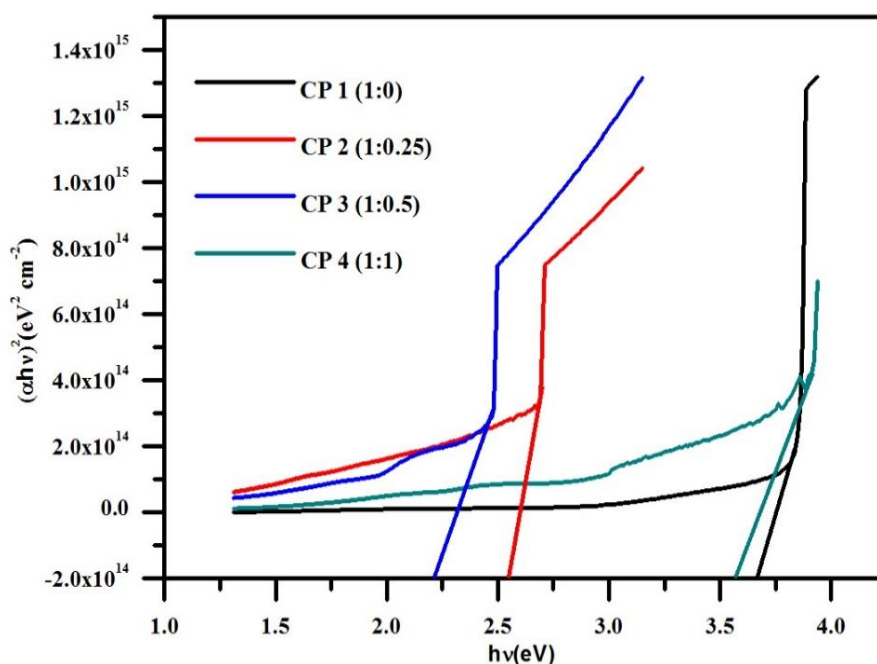


Fig. 4 Band gap of Pristine and CSA doped PDMA thin films

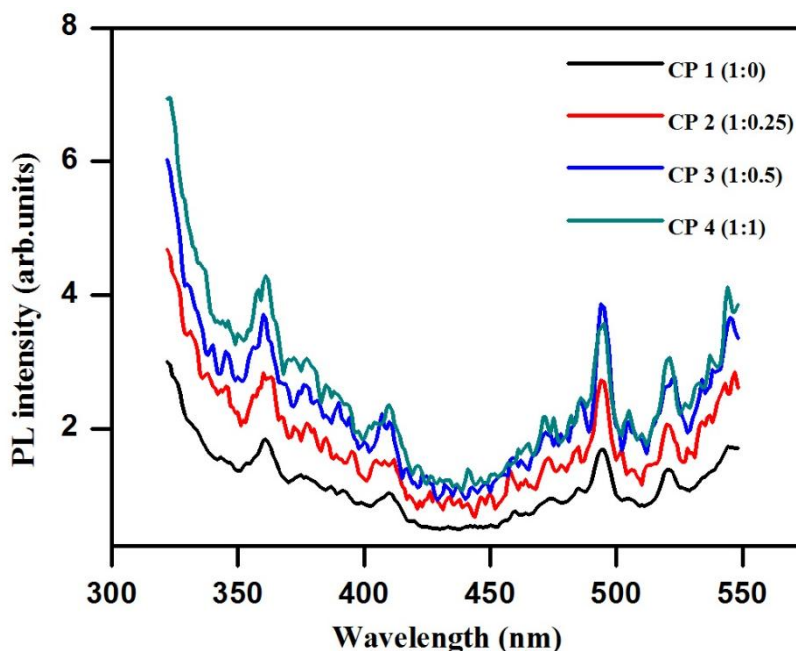




Photoluminescence

The Photoluminescence spectra for the samples CP1, CP2, CP3 and CP4 are shown in the Figure 5. The samples were excited with the wavelength of 300nm. CSA doped PDMA films shows sharp and defined peak in UV and visible region particularly at 360nm and 496nm which are attributed to $\pi \rightarrow \pi^*$ and polaron $\rightarrow \pi$ transition [37]. A small peak observed around 410 nm for the samples particularly higher dopant concentration of the polymer and the occurrence of the peak marked an impression of semiconducting nature by Shimano et al (2015). Sharp peaks were noticed at 520 nm comparing to EB to be crystalline nature of PDMA. Thin films of PDMA with different concentration of CSA showed enhanced PL spectra which are in regular alignment of Benzenoid and Quinoid units to prefer the exciton generation and extension of delocalization length of an exciton and also higher extent of π conjugation [37].

Fig. 5 PL spectrum of Pristine and CSA doped PDMA thin films



Functional group confirmation

The FTIR spectrum of pristine and CSA doped PDMA thin films with the wavelength range of 4000cm^{-1} to 400cm^{-1} are shown in the Figure 6. The protonation of nitrogen bond a band at 3326cm^{-1} occurred in the formation of N-H bonds which is noticed only for CP3 thin film. Due to the stretching vibration of aromatic C-H bonds a band at 3067cm^{-1} and a weak peak at 3059cm^{-1} noticed for CP4 thin film[38]. The peaks at 1142cm^{-1} , 1147cm^{-1} , 1144cm^{-1} for CP2, CP3 and CP4 were observed as conductivity band degree of delocalization of electrons in the polymer chain [36].

The absence of these peaks for EB thin film (CP1) indicates the insulating nature of PDMA. The red shift has been observed for dopant levels for CP2 and CP3 and blue shift for CP4 which has been supported by DC conductivity of the samples. The bands around 1600cm^{-1} and 1500cm^{-1} were assigned to C=N and C=C stretching modes of Quinoid (Q) and Benzenoid (B) rings of the



polymer PDMA [26]. The bands at 1575 cm^{-1} , 1564 cm^{-1} , 1599 cm^{-1} and 1564 cm^{-1} were accredited to the Quinoid (Q) rings of PDMA illuminating the influence of CSA with increasing concentration. Comparing EB and CP2, the peaks of the Quinoid ring shows a shift from 1575 cm^{-1} to 1599 cm^{-1} and 1140 cm^{-1} to 1147 cm^{-1} suggest that during protonation CSA is alienated into proton H^+ and camphor sulfonate ion, where H^+ joined to the imine groups about the Quinoid ring which is promoted by the acidic m-cresol [35][38]. The bands at 1504 cm^{-1} , 1513 cm^{-1} and 1511 cm^{-1} due to Benzenoid rings of pristine (EB) and CSA doped PDMA which have red shift compared to EB.

The bands at 1028 cm^{-1} in CP1 indicates the presence of methoxy groups in PDMA. The bands at 1031 cm^{-1} , 1032 cm^{-1} , 1028 cm^{-1} confirms the existence of $-\text{OCH}_3$ group in the polymer [19]. The band around 1462 cm^{-1} assigned to asymmetrical bonding vibration of the methoxy groups [39]. The intensity ratio of Quinoid ring to Benzenoid ring for CP2 and CP3 where about unity which explains Emeraldine form of PDMA with enhanced electrical conductivity [27]. The bands around 1280 cm^{-1} to 1300 cm^{-1} are pertaining to the existence of aromatic amine unit in the polymer and stretching vibration of C-N. The peaks at 1295 cm^{-1} , 1298 cm^{-1} , 1294 cm^{-1} and 1303 cm^{-1} supports the existence of aromatic amine unit and stretching vibration of C-N [24]. The band at 1111 cm^{-1} , 1118 cm^{-1} observed only for CP2 and CP3 thin films which refers to protonation leading to conducting ES-PDMA [19], the presence of sulfate ion and sulfonic acid group were confirmed by the peaks around $1090\text{--}1100\text{ cm}^{-1}$ and $620\text{--}625\text{ cm}^{-1}$ [40].

DC conductivity:

Electrical conductivity of the pristine and doped PDMA thin film coated on a FTO substrate was measured in room temperature like voltage, current and resistance of the thin films have been measured. The specific resistivity of the samples were calculated using the following equation shown below as;

$$\rho = RA/L$$

where R is the resistance of the thin film measured, A is the cross sectional region of the film and L is the thickness of the film. For the thickness of the film was maintain approximately $1\mu\text{m}$. the DC electrical conductivity of the pristine and CSA doped PDMA are shown in the Table 1. The DC conductivity of the CSA doped PDMA for the ratio 1:0.5 is compared with the other values it seems to be high than the optimum value for maintaining the linear structure of polymer matrix. The higher concentration of CSA dopant leads to more number of CSA-PDMA bond which is disturbing the linear structure of the main chain in PDMA. It is identified as 1:0.5 ratio of optimized value for the further study of CSA – PDMA thin films.

Table 1
DC Conductivity of pristine and CSA doped PDMA thin films

S. No	PDMA-CSA ratio	Conductivity S/cm
1.	CP1 (1:0)	1.45×10^{-7}
2.	CP2 (1:0.25)	1.62×10^{-5}
3.	CP3 (1:0.5)	3.25×10^{-2}
4.	CP4 (1:1)	1.91×10^{-4}



Conclusion

For the first time, the Camphor sulfonic acid doped Poly (2, 5-dimethoxyaniline) thin films were fabricated by spin coating technique. Poly (2, 5-dimethoxyaniline) have been synthesized by oxidative polymerization and doped with dissimilar mass ratio of CSA and the principle investigation was done. From UV-V spectra, the optical band gap was calculated and the values like 2.55 eV, 2.21 eV, and 3.56 eV for CSA doped PDMA thin films. The crystalline nature of the CSA- PDMA thin films were recognized through their XRD pattern. The functional groups have been identified by FTIR spectrum. Semiconducting nature of the thin films were confirmed by PL spectrum optimization of doping level to identify the DC electrical conductivity. Hence, it is concluded as simple, low cost, high crystalline Camphor sulfonic acid doped Poly (2,5-dimethoxyaniline) of thin films which can be employed as 'p' type material in active layer, cathode and buffer layer in organic solar cells, DSSC and in gas sensors.

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