The optical properties of polyaniline (PAni) prepared by chemical method

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Abstract

Polyaniline (PAni) was syntheses by oxidation chemical polymerization method. Formic acid with weight ratio (5-50)% used to doped PAni,The optical properties was measured with UV-Spectra photons. The optical data analyses to found energy gap for all ratio.

Introductio

Intrinsic conducting polymers(ICP) offers great technological application such as , static films for transparent packaging of electronic components[1]. Electromagnetic shielding [2]. Recharge able batteries[3] light –emitting diodes[4]. Protection against corrosion[5]. Conducting paints and glues[6].

Poly aniline (PAni) , occupies the most important place among the conducting class of polymers[7]. Polyaniline is atypical phenyl based polymer having chemically flexible-NH-group in the polymer chain flanked by phenyl ring an either side[8].It is represents a class of macro molecules whose electrical conductivity can by varied from on insulator to conductor by the redox process[9].The conducting state of polyaniline is easily obtained by simple protonation by reacting with acids and the process is also reversible. The availability of wide rang of dopant such as. Mineral, carboxylic and sulfonic acids make the polyaniline chemistry much move interesting for controlling the various properties such as solubility,soild state ,ordering, micro and nano-sized materials etc[10-11].

Experimental Method

polyaniline was synthesized by the oxidation polymerization of aniline in acidic media. Using a method similar to the reported by (M.Jayakannan (2006) [12].Distilled aniline (0.0274 mol) was dissolved in (0.1 M) HCL and taken in a three necked flask and cooled to (0^0C) using ice . to this a pre-cooled solution of (0.0343 mol) ammonium persulphate in (0.1M) HCLwas added slowly very carefully after 5 min green colored polyaniline-HCL was started to precipitate from the solution. The polymerization was further proceeded by stirring at 30^0C for 24h.

The precipitate was filtered washed with (0.1M) HCL for three time and stirred in a flask containing (0.1M) a aqueous ammonia solution (112.5 ml) the blue precipitate was stirred for 3h at room temperature to ensure the completion of de-doping the resultant blue emeraldine base was filtered, washed successively with water , methanol and acetone .it was dried in a vacuum oven at 80^0C for 12h . Powder polyaniline was dissolved in DMSO . the solution of (PAni) added on the formic acid solution as drops with moving stirrer the weight ratios of formic acid were (5%,10%,15%,20%,25%,30%,405,50%).

The last process was dropping the mixture on broad of glass and leaved to dry for 48h . The absorbance and transmittance before and after doping were studied at the range(200-900nm) using the (UV) spectrophotometer. The measurements were adopted at room temperature and to be analyzed and discussed.

Results and discussion

The characterization of undoped and doped (PAni) film have been curried out using IR analyzing technique as shown figure(1) and(2) respectively. Table (1) tabulated the wave vector of functional groups of (PAni). The doping appear at wave vector(1735)cm^{-1} , Which is refer of C=O group of formic acid(CH_3COOH), That group   agreement   with [20].The group at PAni agreement with [20-21].
The absorption coefficient ,α, is written as[13-14]

$$\alpha = (\tfrac{2.303}{d})(A + \log(1 - R)^2) \ldots\ldots\ldots\ldots (1)$$

where A is the absorbance (A= - logT),T is the transmutation, d the thickness of the film

The Absorption coefficient was estimated after correcting for reflection losses[13]. Fig(3) show the absorption coefficient(α) as a function of photon energy ,hν, of different specimen (undoped PAni, 5%,10%,15%,20%,25%,30%,40%,50%). All specimen show systematic behavior varies photon energy, hν, . The absorption data were analyzed for evidence of inter band transition in fundamental absorption region. The data was fitted to one-electron theory of Bardeen et al [15] in order to obtained information about the direct and in direct band gap[16]. For high absorption coefficient α > 10^3 that refer to direct transition[15, 16].

$$\alpha = \frac{A(h\nu - Eg)^{1/2}}{h\nu} \ldots\ldots\ldots\ldots (2)$$

where A is constant independed of photon energy and depending on the probability of transition and Eg direct energy gap. Figures (4,5,6) show the photon energy dependence on (hνα)^2 for undoped and doped PAni respectively . The plot of(hν α)^2 agent hν yields a straight line for value of   α >10^3 which show good fit with eq.(2) , extrapolation of the straight line to α =0 gives the direct energy gap , which are tabulated at (Table 2).

Fig(7) shows direct energy gap as a function of different weight ratio of formic acid. The curve show that the energy gap decrease with increasing the weight rate of doping (formic acid), because the doping create polaron states in band gap and that is increase with increase doping then become a polaron band between valance band a conduction band for all details about a mechanism of conductivity in conducting polymers [17]. That result was agreement with[18-19] .

Conclusion:

   Poly Aniline synthesis by chemical polymerization, then doped with different ratio of formic acid. The polymer was characterizes by IR in order to show doping . The optical properties show direct energy gap. This gap decreases with increases doping. So that the doping increase the conductivity in polyaniline.

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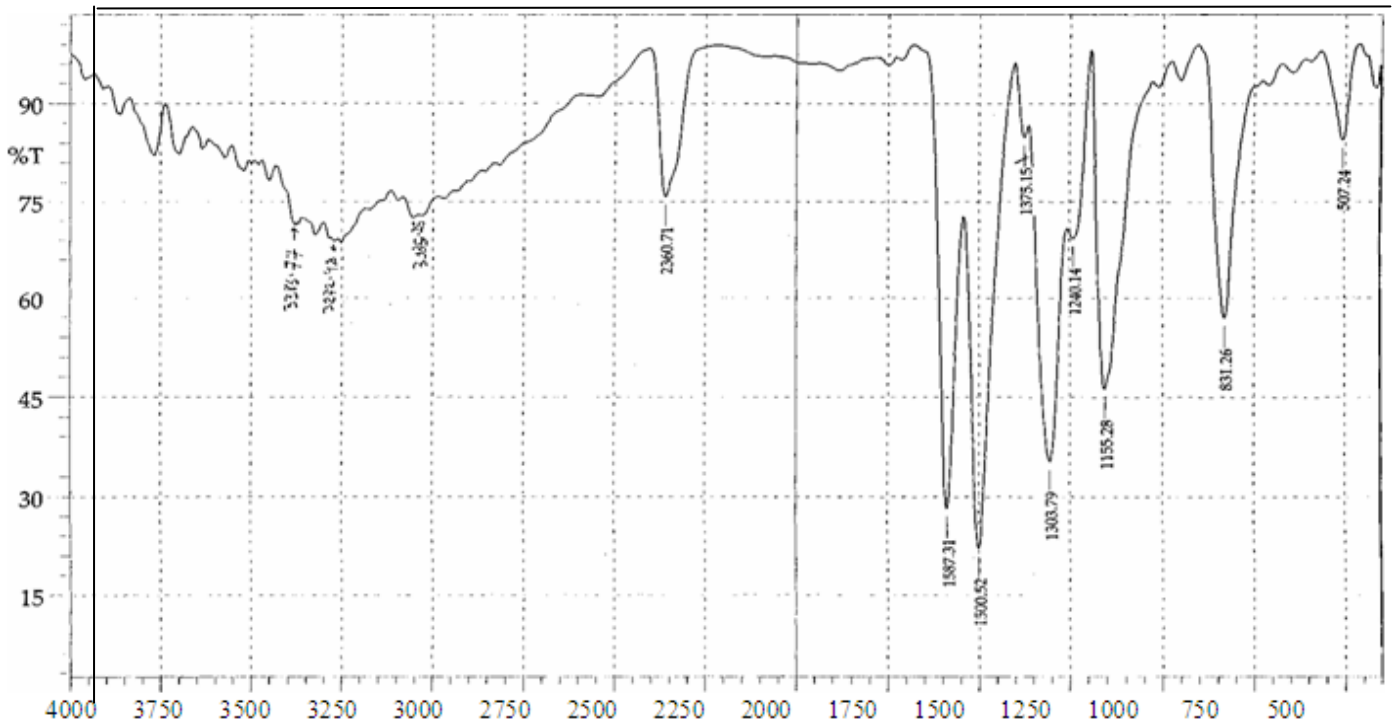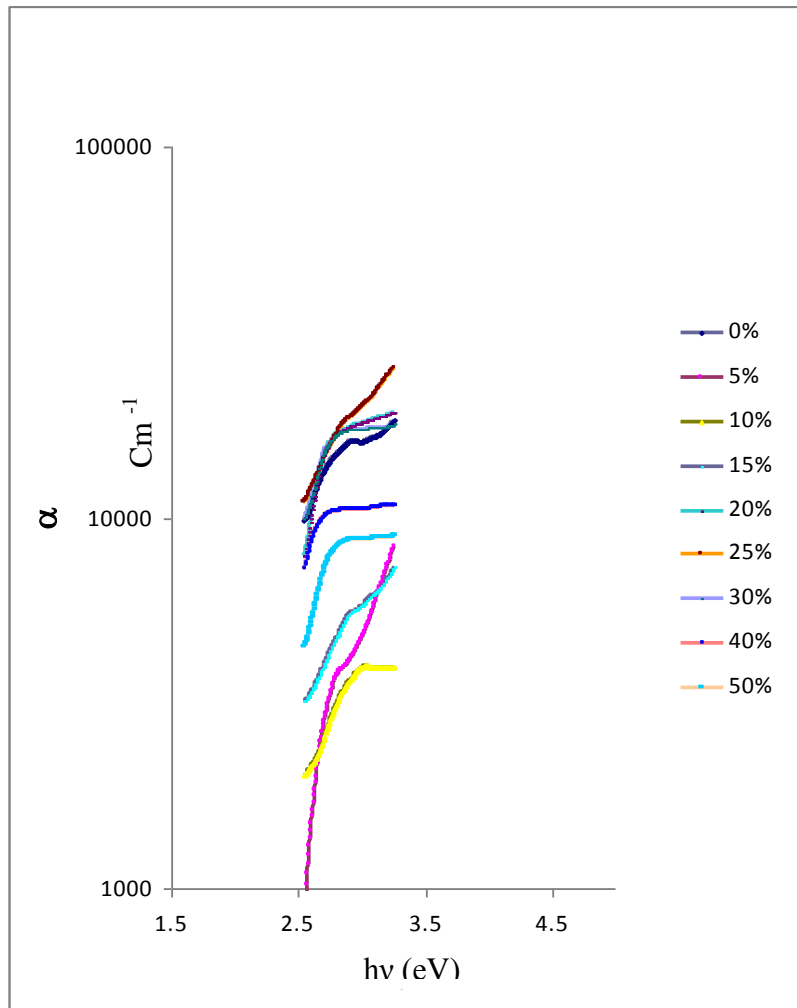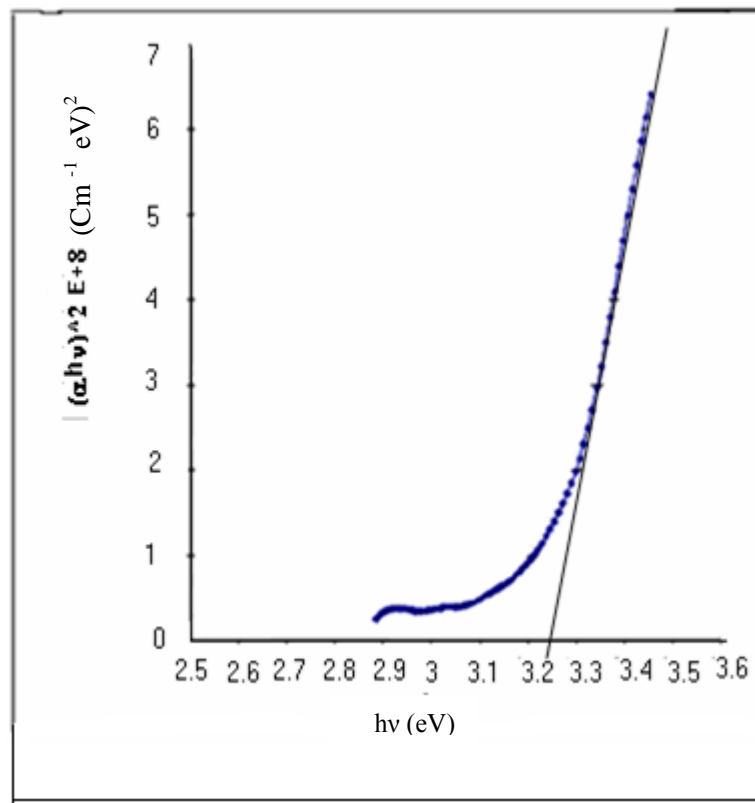
Fig(1): IR for undoped Polyaniline
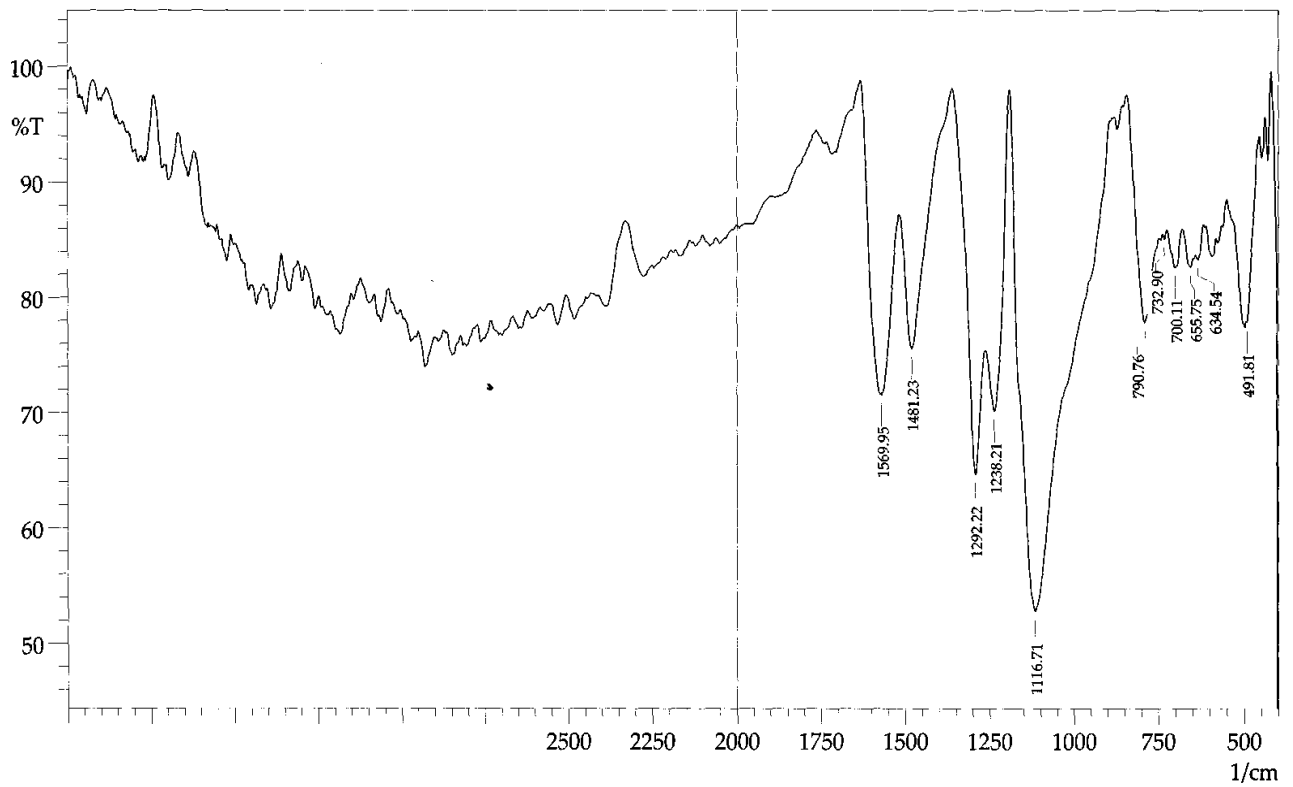
Fig(2) IR for doping polyaniline

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Table (1) The fictional group of PAni

| C=C Benziod	C=C Quinod	C-N	C=O	C-H	Functional group of PAni
1500	1587	1303	-	831	Functional group of undoped PAni
1481	1569	1292	1735	790	Function groups of doped PAni
1500 1483	1583 1567	1250	-	-	Ref.[20]
1485	1572	1299	-	805	Ref.[21]
1503	1599	1308	1744	783	Ref.[22]

Fig(3):The absorption coefficient of undoped and doped(PAni) as aversus of photon energy for oll doping ratio.

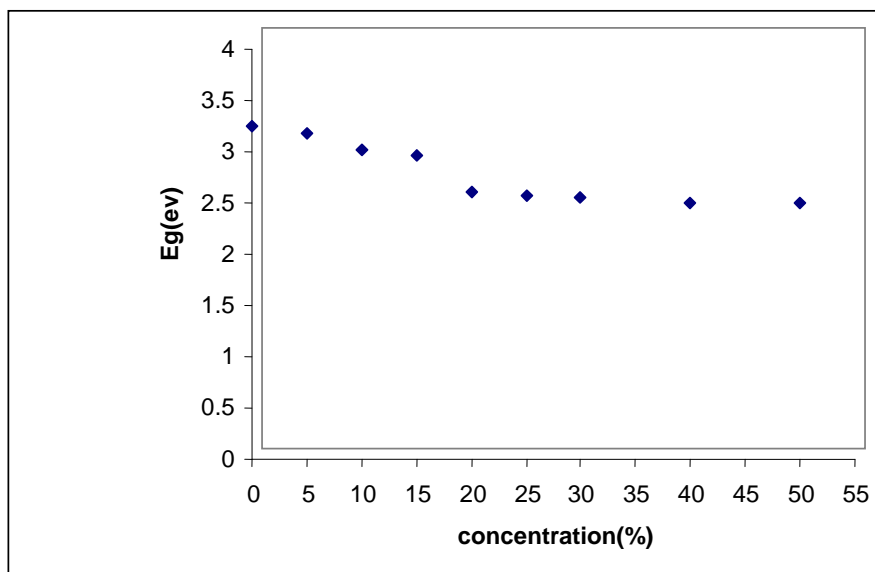Fig(4) $(\alpha h\nu)^2$ vs. photon energy for undoping poly aniline
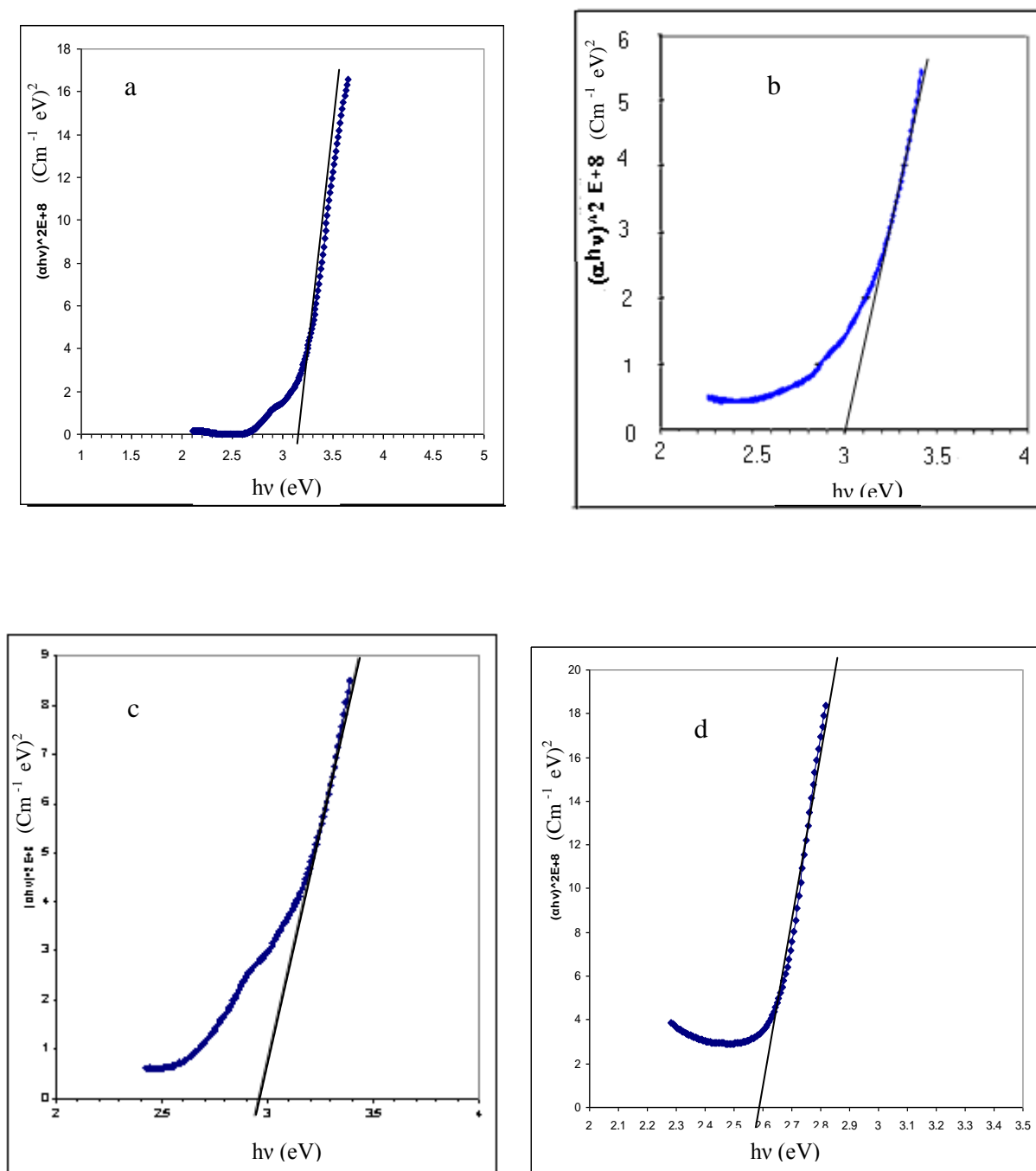
Fig(5):$(\alpha h\nu)^2$ vs. photon energy for doping poly aniline
a) 5%   b) 10%   c) 15%   d) 20%
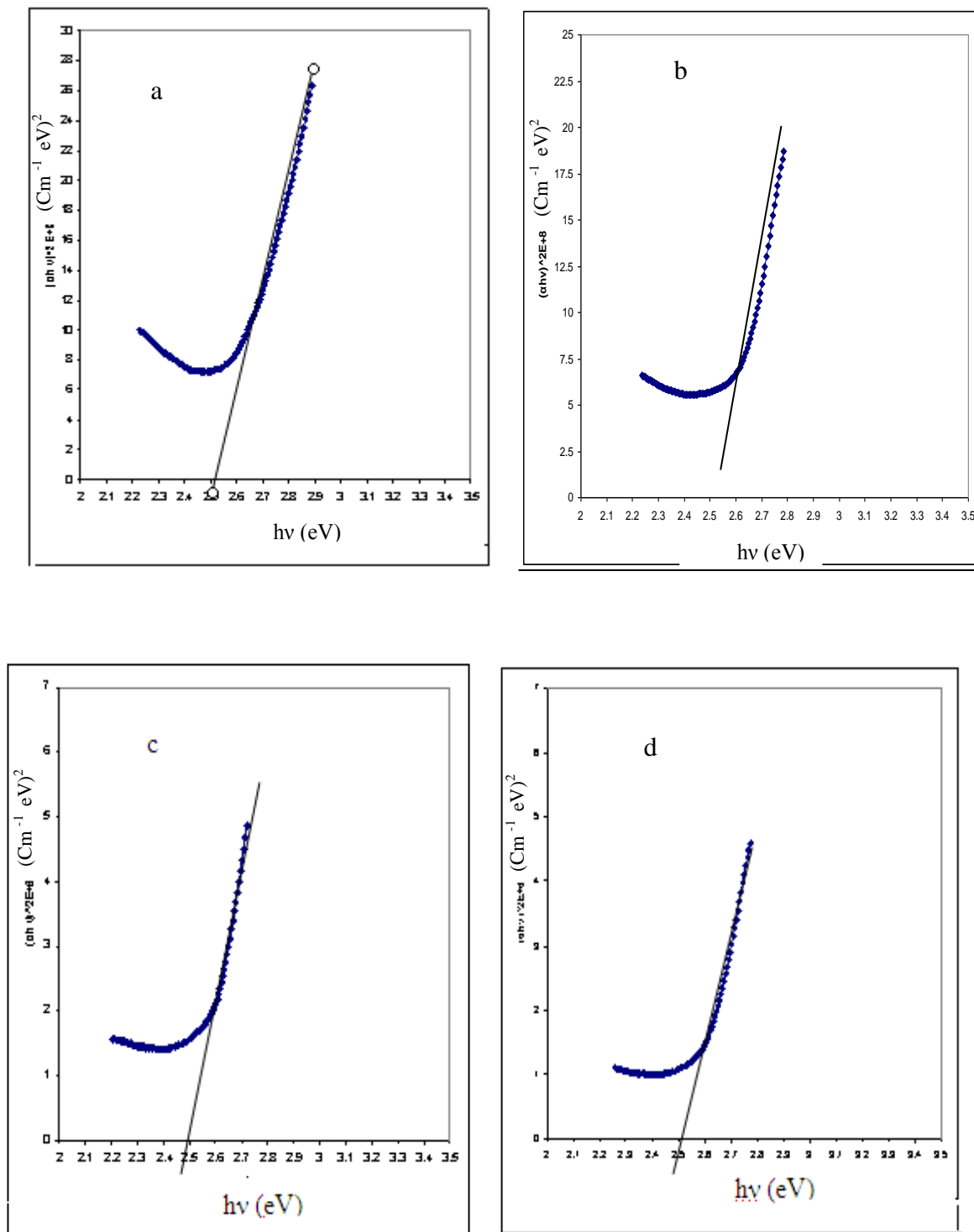
fig(6): (αhν) 2 vs. photon energy for doping poly aniline

a) 25%   b) 30%   c) 40%   d) 50%

Fig(7): The energy gap Eg of doped PAni with weight ratio of Formic acid

Table (2): Show the energy gap Eg of doped PAni

concentration of formic acid	Eg(eV)
% 0	3.25
% 5	3.18
% 10	3.02
% 15	2.98
% 20	2.6
% 25	2.58
% 30	2.56
% 40	2.5
% 50	2.5