

PHOTOLUMINESCENCE, STRUCTURAL AND ELECTRICAL INVESTIGATIONS OF KITON RED 620 ORGANIC DYE DOPED POLYANILINE.**Anand Kumar^{1*}**^{1*}Department of Physics, Pt. Neki Ram Sharma Government College, Rohtak -124001 (India)**Abstract**

The present work reports the synthesis of pristine polyaniline and Kiton Red 620 organic dye composites synthesized by in situ chemical oxidative polymerization with potassium dichromate as an oxidant in aqueous hydrochloric acid medium and chemical doping of Kiton Red 620 in polyaniline with different concentrations. The synthesized polymeric composites were characterized by Photoluminescence spectroscopy, X-ray diffraction and dc conductivity measurement techniques. Photoluminescence spectra confirm excellent electrooptical properties of prepared polymeric material, while X-ray diffraction patterns exhibit amorphous behavior leading towards semicrystalline, as most conducting polymers have. For electrical investigations, dc conductivity has been measured by two probe method within temperature range 300-400 °K and significant enhancement in dc conductivity has been observed simultaneously with increased in temperature; confirming semiconductor nature of synthesized polymer composites.

Keywords: Polyaniline, Kiton Red 620, X-ray diffraction, dc conductivity.***Corresponding author e-mail:** akdmdu@gmail.com**1. Introduction**

The conducting polymers since their discovery by MacDiarmid et. al. [1], got an influential and remarkable attention in scientific community as their amazing applications in modern society are unmatched. Conductive polymers like polyacetylene, polyaniline, polythiophene, polypyrrole, polymethylmethacrylate (PMMA) etc. have been extensively studied due to their scientific and technological applications and future prospects based on easily adaptable optical and electronic properties[2-3]. Among mentioned conductive polymers, Polyaniline in its emeraldine base (EB) oxidation state has specific magnetic, electronic, thermoelectric, electrical and optical properties [3]. Polyaniline is popular also due to its good environmental stability, processibility, electrical conductivity, efficient potential applications like LEDs, FETs, catalysis, batteries, separation membranes, EMI shielding, sensors, corrosion control, secondary batteries etc. and commercially relatively low-cost preparation [4-6]. Apart from above mentioned applications, recently dye doped polymeric materials got attention due to potential applications in optics, lasers atmospheric sensing, photodynamic therapy, optoelectronics, quantum electronics, solar cells, receiving and sending information, Local Area Network (LAN), biomedical applications etc [7-10]. Generally, polyaniline prepared in bulk via chemical or electrochemical methods with oxidized polymerization of monomer

aniline [11], the same process followed in the present work. The insertion and incorporation of organic dye molecules in host polyaniline matrix can scrutinize dye lasing materials in near UV and near IR regions due to tunable property of host in electronic levels as reported by many researchers [12]. The advantage of dye doped organic polymers in comparison of colored inorganic materials are their lower density, low cost, higher radiative stability and flexibility, making them irreplaceable materials in their fields. Modern photoconductive polymers are used as effective convertors of light and electrical energy due to the interaction between electromagnetic interaction and pi electrons of polymer conjugated bonds [12], but they possess less change range in spectral, luminescent, electrophysical and nonlinear optical properties than organic dyes. Same scenario is with solely dye doped materials [10], but the dye doped polymers enable the light radiations properties over a wide spectral range with higher efficiency than polymers and dyes separately. For future exploring prospective we synthesized polyaniline in aqueous acidic medium and then doped it with Kiton Red 620 (organic dye) in different concentrations. The synthesized polymeric samples have been characterized by Photoluminescence, X-ray diffraction and dc conductivity measurement techniques.

2. Experimental

The following chemicals were used for preparation: The aniline (Merck, 99.9 %), Potassium dichromate (S.D. Fine Chemicals, 99 %), Hydrochloric Acid (Qualigens Chemicals, 99 %), Tetrahydrofuran (Merck, 99.9 %), Ammonia solution in water 28 % (S.D. Fine Chemicals), Kiton Red-620 (M.W. 580.66, $C_{27}H_{29}N_2O_7S_2Na$) (Exciton Inc. Dayton, USA)

The prior distilled aniline at 280 K (Merck, 99.9 %) was stirred thoroughly with drop wise addition of potassium dichromate (0.1 M) as an oxidant in hydrochloric acid medium (1 N) as suggested by MacDiarmid [13]. The prepared mixture was cool down at 273 K for completion of polymerization process. The prepared precipitates then filtered, washed with distilled water and treated with aqueous ammonia solution. To get neutral host polymer, samples were treated with distilled water until the neutrality confirmed by both pH paper and pH electronic meter. Dark colored polyaniline powder then dried up to 48 hours in oven by increasing temperature at regular intervals up to 350 K to acquire moisture free host polymer. The dried powder of polyaniline was grinded to very fine and the Kiton Red 620 organic dye with different percentage such as 5, 10, 15 and 20 % (v/v) of concentration (10^{-2} M) taking tetrahydrofuran as solvent have been doped with each 2.0-gram powdered polyaniline in cleaned beakers. Now 5 ml distilled water added in all solutions already prepared with magnetic stirring for 30 minutes. The prepared samples have been dried with vacuum oven at temperature 50 °C for 72 h. Now the prepared samples have been grinded again to obtain fine powder for characterization. X-ray diffractometer (X'Pert Pro PANalytical's) having wavelength 1.5406 Å ($CuK\alpha_1$) was employed for structural analysis of polymeric composites pellets having dimensions of 10 mm diameter, 1 mm thickness, prepared using of hydraulic pellet press (Kimaya, WT-324). The photoluminescence spectroscopy (PL) of the prepared samples have been performed with Hitachi (F-7000) spectrophotometer having range 200-900 nm, while two probe method was employed to measure the dc conductivity of both pristine polyaniline and

dye doped composites in the temperature range 300-400 K with the help of specially designed sample holder with a potential difference of 0-15 V and Pico-ammeter (Keithley, 617).

3. Results and discussion

3.1 XRD studies

The X-ray diffraction is one of the widely used experimental technique to get crucial information about the structure of prepared samples. As per literature review, the structure of polymer not only depends on polymer matrix configuration but also on synthesis route, solvent and ionized state [14]. X-Ray Diffraction of pristine polyaniline, 5 % and 10 % dye doped composites reflect amorphous nature (Fig. 1(a)), while 15 % and 20 % dye doped composites exhibit semicrystalline structure as shown in Fig 1 (b-c).

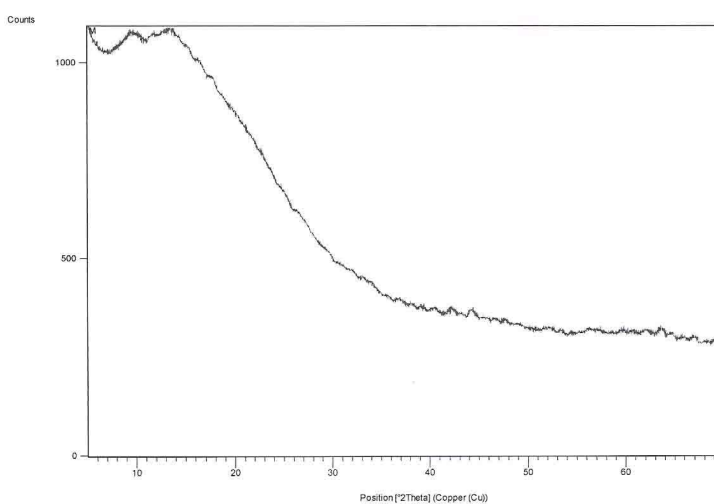


Fig. 1(a)

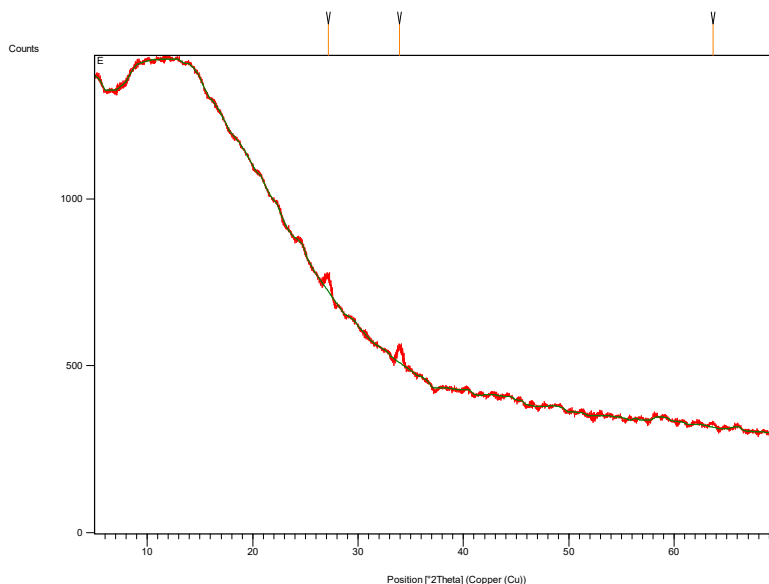


Fig. 1(b)

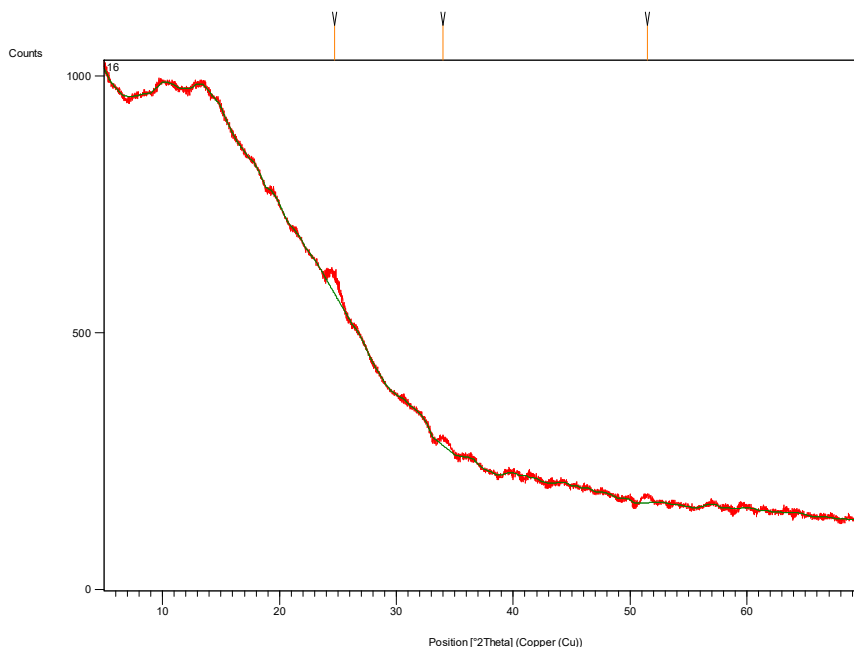


Fig. 1(c)

3.2 DC conductivity measurements

As electrical conductivity which is related to energy band gap, is one of main scientific property have to investigate in case of conducting polymers. In present research work, the dc conductivity measurement was investigated & measured by Keithley Pico-ammeter with help of specially designed pellets sample holder; in the varying temperature range of 27 °C to 100 °C.

The electrical conductivity of an ohmic material is given by

$$\sigma = l / RA \quad (\text{S cm}^{-1}) \quad (2)$$

The electrical dc conductivity of undoped polyaniline has been found to be $3.2 \times 10^{-8} \text{ Scm}^{-1}$ and $5.4 \times 10^{-7} \text{ Scm}^{-1}$ at 27 °C and 100 °C respectively. In case of 5, 10, 15 and 20 % (v/v) Kiton Red dye doped samples, the conductivity is found to be 6.78×10^{-7} , 4.45×10^{-6} , 8.80×10^{-4} and 9.56×10^{-3} respectively. So, electrical characterization measurements confirms the semiconducting behavior of composites as dc conductivity increases with increases in temperature. We may explain this behavior as: At low doping levels, the charge carriers may self-localized with nonlinear configurations and the heavy doping forced the wave functions to delocalized along polymer matrix; resulting increase in conductivity significantly [15]. The protonation may be another cause for variability in electrical conductivity of polyaniline as suggested by MacDiarmid et al. [16].

3.3 The photoluminescence spectroscopy: The luminescence is ‘cold light’ from other sources of energy, which can take place at normal and lower temperature. It is one of the best and efficient mechanism of light emission as the output per unit energy input is very high than incandescence and this process is extremely useful for detection of contaminants, monitoring the progress of reaction, conformation, configuration, intermolecular energy transfer, stabilization and radiation damage. The PL spectra of undoped and 5, 10, 15, 20 % dye doped polyaniline (PANI) shows relative heights of the emission peaks increases with the different concentration of dopant mixture as shown in Fig.2 (a-e).

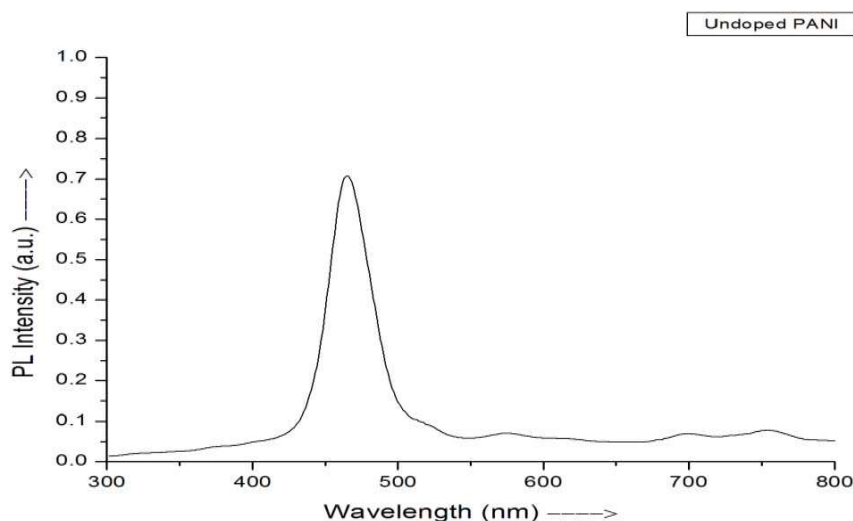


Fig. 2 (a)

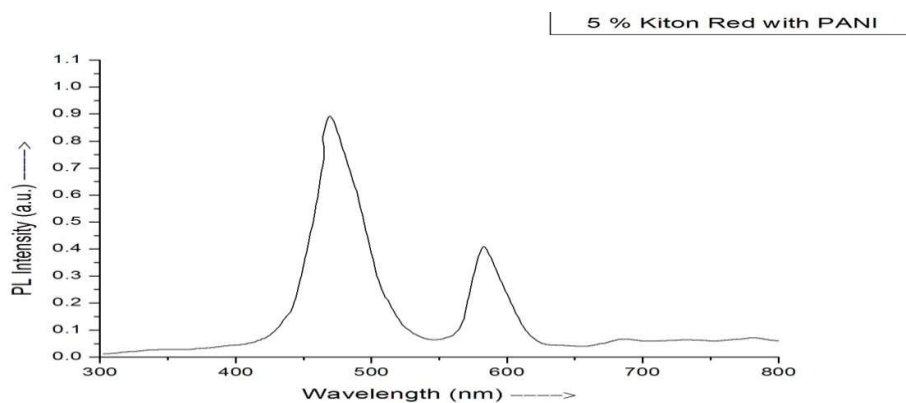


Fig. 2(b)

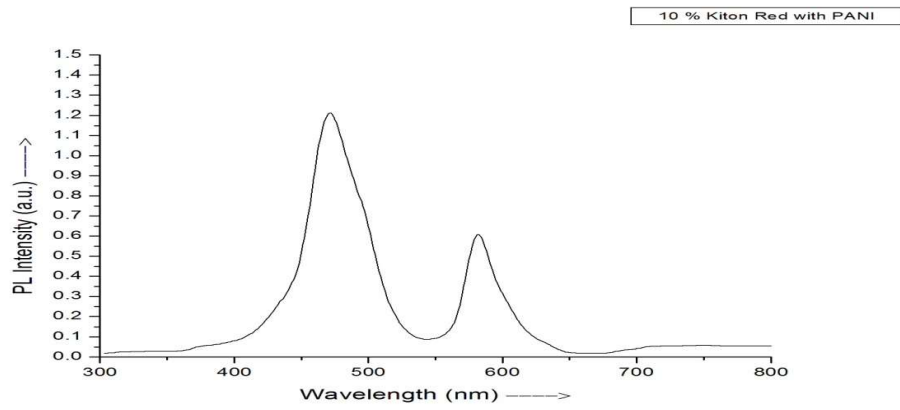


Fig. 2 (c)

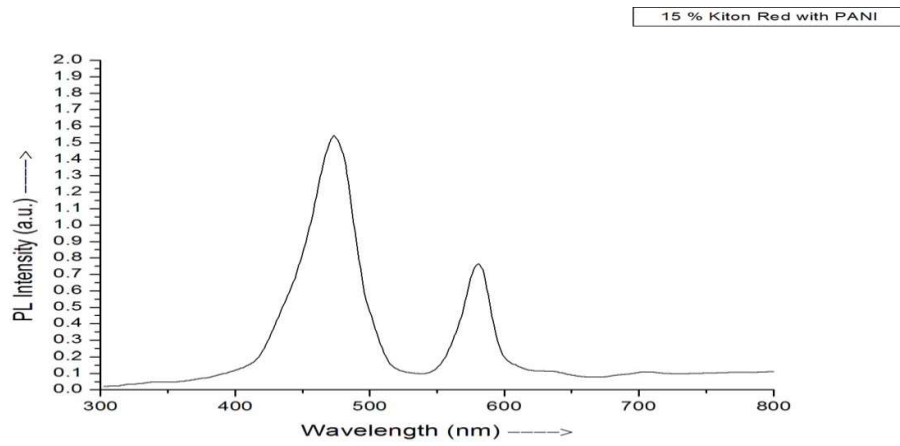


Fig. 2 (d)

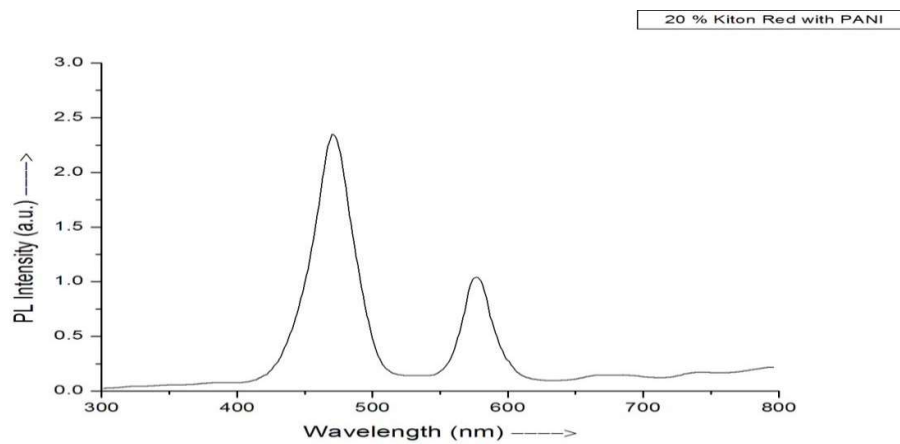


Fig. 2 (e)

It has been noticed that single intense peak appeared around 460 nm in case of undoped polyaniline, while two intense peaks have been observed around 460 nm and 575 nm in case of doped composites, getting intense continuously with increasing dopant concentration. These increases in intensity with sharp peaks of emission can further suggest the doping worth showing the photoluminescence behavior of doped π -conjugated polymers. As the emission peak \sim 575 nm appeared in yellow spectral region, so dye doped polymer matrix can be used in passive mode locked lasers and laser amplifiers. Also it is known that emission spectra of polymers depend on many factors like polymer size, nature of solvent, polymer dopant concentration etc. [17]. The PL spectra of samples follow general trend in shape indicates the excellent tuning of dye with polymer matrix. As per standard record, the dye has maximal absorbance around 565 nm and present characteristic investigation proved too; so, it is good structural and optical material for polymeric electrooptical applications [18]

4. Conclusions

The polyaniline polymeric composites with doping of organic dye (Kiton Red 620) have been prepared by chemical oxidation polymerization method. From characteristic investigations, we conclude that the doping induces structural, electrical and chemical changes in the conjugated polymer, which leads to the changes in optical and electrical properties significantly. The band gap of composites has been found to decrease with increase in dopant concentration. The prepared polymer composites are semiconducting in nature as their conductivity increases with increase in temperature. The photoluminescence spectra (PL) of pristine polyaniline exhibits excellent tuning of dye with host polymer matrix.

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