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An Investigation on Influence of Gamma-Irradiation and Doping on Chemical Structures and Optical Properties of Conducting Polypyrrole

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Abstract

In this study, the authors report on effect of gamma-irradiation and doping (bromine, iodine and sulfate ion) on chemical structure and optical, electronic properties of polypyrrole. Optical absorption spectrum of PPY shown absorption bands centered around 36.2.5 nm (peak 1), 450 nm (peak 2) and 525 nm (peak 3) positions. Gamma irradiation resulted in broadening of peak A together with a band shift of 45–525 nm and disappearance peaks 2 & 3. Doping of bromine and iodine resulted in disappearance peak 1; while shifting of peak 2 (462.4 nm in case of bromine and 470 nm in case of iodine and 460 nm in case sulfate ion) is observed. Regarding peak 3 shift, peaks to 625 nm (sulfate ion) 685 (bromine), 625 (iodine) are observed. FTIR spectrum pristine PPY exhibited absorption bands centered around 3904–3447 (N–H strong Vibration), 2900 (C–H Vibration of CH_2/CH_3), 2333 (–N (+ = C–) 1719 (C=O), 1655 (conjugated groups), 1560–1528 (Aromatic N–H & C=O Vibration) 1024 (Five remembered ring vibrations) suggesting the chemical of its composition. On irradiation, the band position and intensities considerably varied, suggesting that irradiation caused severe damage to chemical structure. Doping of PPy also caused band shifts and variations in band intensities. Optical properties – like optical band width and refractive index values – are evaluated. Conductive nature of PPy is verified by recording cyclic–voltamertic data which suggest oxidation & reduction property of conducting polymers. The data suggest both gamma-irradiation and doping can be used for sensor applications.

Keywords: Polypyyrole (PPy), gamma irradiation, FTIR, Bandgap (Eg), refractive index (n)

INTRODUCTION

Polypyrrole (PPy) is considered to be an intrinsic conducting polymer finding applications as electrode material in lithium–ion batteries [1], bio-sensor/electronic material [2], controlled drug delivery [3] and important material in smart fabrics. PPy has unique properties of thermal and environmental stability, process ability enhancing its applications. Electronic properties of PPy are tunable by doping or by radiation treatment.

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SCOPE OF PRESENT STUDIES

Although effect of gamma-irradiation and doping of PPy is attempted, the authors focus attention on the following aspects:

1. The PPy is an intrinsic conducting polymer, and its conductivity can be tunable by or by irradiation to enhance its applications.
2. The literature reports indicate effect of irradiation and doping on PPy and comparative studies are not available.

3. Therefore, the present studies aimed to focus on comparison studies of effect of gamma-irradiation and doping (different dopants like bromine, iodine and sulfate ions) on chemical and conductive properties of PPy.
4. The optical properties – like band gap and refractive index – are calculated and the values are compared.
5. The process of oxidation and reduction are studied using cyclic voltammetry technique.

EXPERIMENTAL

Polypyrrole (PPy) in the form of films is synthesized by electro chemical method and used as it is. Optical absorption spectra of PPy films are recorded on Shimadzu 5000 model spectro photo meter with empty window as reference. FTIR spectra are recorded on PERKIN–ELMER SPECTROMETER for powder samples of PPy by mixing it with potassium bromide (K Br), with pellet thickness being 1–2 mm. Gamma irradiation are carried out using Cobalt-60 radiation source with a dose rate of 0.15 K Gy/hr in air at room temperature. Doping has been undertaken during synthesis of PPy itself with standard procedures as described in literature.

RESULTS AND DISCUSSION

Optical Absorption

Optical absorption spectra of pristine PPy is shown as curve A in Figure 1. The spectrum consists of absorption bands centered around 362.5 nm, 450 nm and 525 nm designated as P1, P2, and P3, respectively. The first peak (P1) is assigned pi–pi* transition of aromatic groups [1]; while peak P2 and Peak P3 are assigned to polaronic species that are normally present in conducting polymers. Gamma irradiation of PPy resulted in shifting (450–525 nm) of P1 together with broadening. Therefore, peak 1 is expected to diminish; while peaks 2 & 3 (P2 & P3) might have been merged as shown in Curve E in Figure 1. The results suggest that the backbone of PPy is severely damaged by irradiation. Doping of PPy with sulfate ion (shown as curve B in Figure 1), bromine (shown as curve C in Figure 1) and iodine (shown as curve D in Figure 1) resulted in disappearance peak1; while shifting of peak 2 (450–462.5 nm for sulfate doping, 450 nm to 470 nm for bromine doped PPy and 450–460 nm for iodine doped PPy). Shifting of peak P3 is also observed (for sulfate doped PPy 525 nm–625 nm, bromine doped PPy 525–685 nm and 525 to 625 nm for iodine doped PPy). The band shifts in case of doping are expected as dopants (sulfate, bromine and iodine) are expected to react with chemical groups of PPy promoting unsaturation along its backbone.

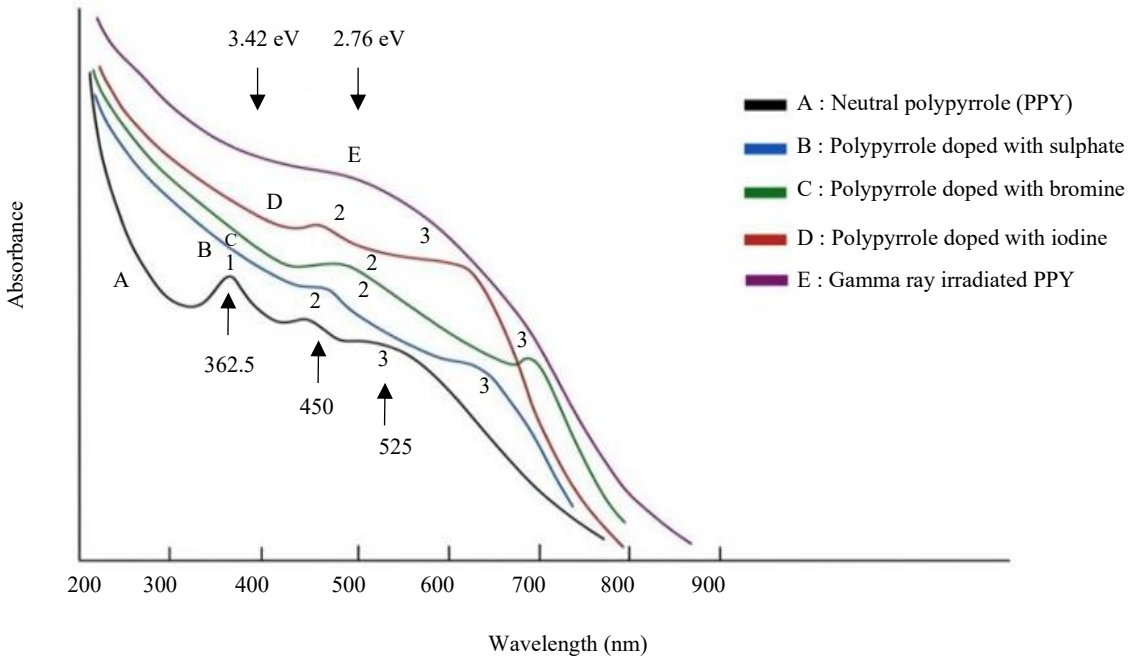

Figure 1. Optical Absorption of Polypyrrole.

Using optical data, the parameters – like band gap (Eg) and refractive index – are evaluated as given in Table 1 (Table Optical properties of PPy under different conditions).

Table 1. Optical absorption of PPy

Polymer	Band 1/peak (P1)	Band 2/peak 2 (P2)	Band 3/peak 3 (P3)
Pristine PPy	362.50 nm	450 nm	525 nm
Sulphate doped PPy	–	462.5 nm	625 nm
Bromine doped PPy	–	470 nm	685 nm
Iodine doped PPy	–	460 nm	625 nm
Gamma irradiated PPy 15 minutes irradiated	450–525 nm	–	–

Regarding analysis of optical bands, the band P1 is assigned to pi–pi* transition that is normally present in most of the conducting polymers due to the presence unsaturated groups present in PPy chains [1, 4]. The second band P2 and third band observed at 450 nm and 525 nm are due to the presence of polarans and bi-polarans present in PPy.

1. *Effect of Sulfate Ion Doping:* When sulfate ion was doped to PPy, the band P1 almost disappeared while P2 and P3 were shifted to longer wavelengths 462.5 nm and 685 suggest increase of conjugation in the polymer. Or structural additions. The results suggest that sulfate ions react with PPy chains, causing both shifts as the shifts are in the order of 2.5 nm and 10 nm, respectively.
2. *Effect of Doping of Bromine:* Doping of Bromine caused shifting/merging peak P1 with P2 and P2 has red-shifted to 470 nm while P3 is shifted to 685 nm. Therefore, a shift of 20 nm and 160 nm were noticed for P2 and P3 peaks. The peak shifts suggest enhancement in conjugation of PPy together structural changes.
3. *Effect of Doping of Iodine:* For iodine PPy also P1 merged with P2 and position of P2 and P3 were shifted to 469 nm (shift of 10 nm) and 625 nm (shift of 100 nm), respectively. Therefore, doping of PPy caused electronic as well as chemical structural changes.
4. *Effect of Gamma Irradiation:* Gamma irradiation resulted in merging of P1 with P2 and a broad absorption band extending from 450–525 nm was observed. As this region corresponds to P2 and P3 and without P1, the pi–Pi* structure of PPy is expected to be damaged by irradiation. But merging of P2 and P3 with increase of intensity indicate enhancement in unsaturation is predicted.

Calculation Refractive Indices Using Band Width Data

Using Talc plots the values of band gap (Eg) under different conditions are evaluated. The Eg values are used to calculate refractive index values under different conditions as given in Table 2.

Table 2. Evaluation of Eg and refractive index values.

Condition	Peak 1		Peak 2		Peak 3	
	Eg (eV)	*n*	*Eg (eV)*	*n*	*Eg (eV)*	*n*
Pristine	3.42	1.95870068	2.76	2.09251678	2.36	2.16454928
Sulfate			2.68	2.112808	1.98	2.29370258
Bromine			2.64	2.00866201	1.81	2.37659449
Iodine			2.69	2.11031251	1.98	2.29370256
Gamma irradiated			2.54	2.29370258		–

Variation of Eg and n Value

To have a comparison in Eg and n values histograms are plotted in the form of histograms as depicted in Figure 2.

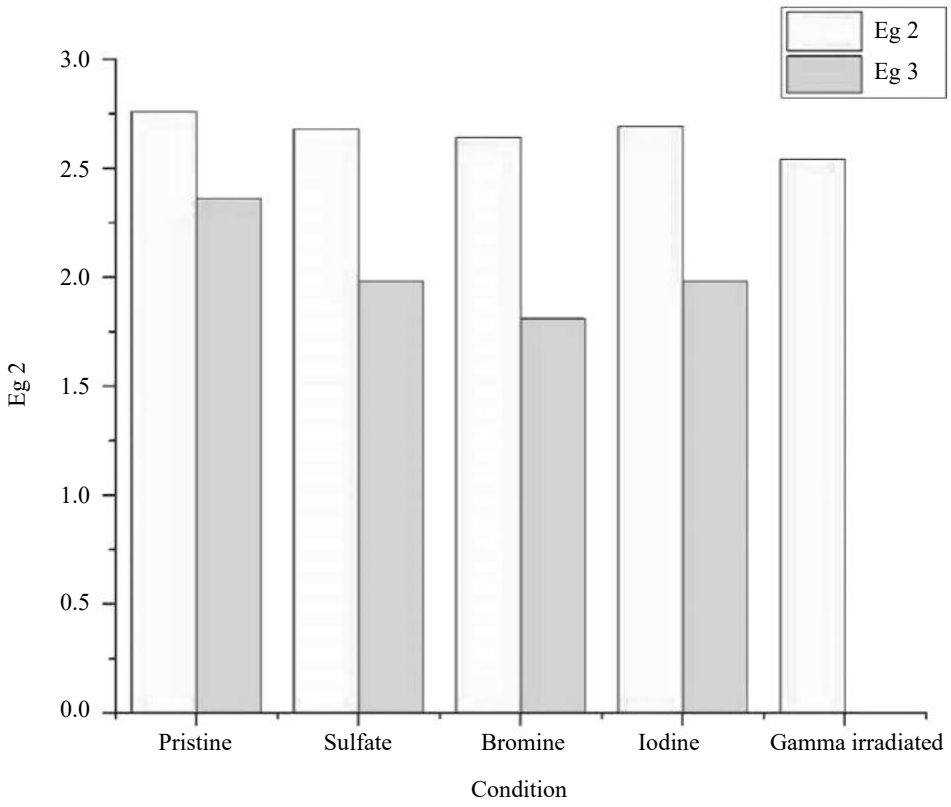

Figure 2. Comparison of condition Eg values.

Variation of Condition and n Value

To have a comparison of condition and n values histograms are plotted in the form of histograms as depicted in Figure 3.

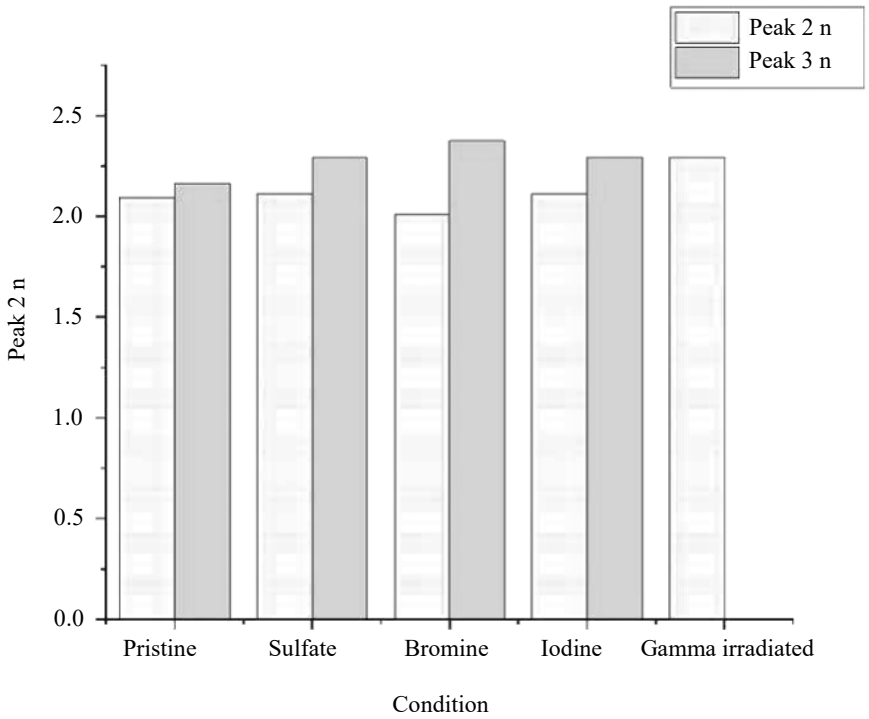

Figure 3. Comparison of condition and n values.

Reasons for Variation in Optical Data

Gamma irradiation/doping of polymer results in cleavage of molecular chains leading to either chain scission/crosslinking or generation of defect sites. All these factors cause broadened optical bands with red shift (shifting of wavelength to higher scales) and decrease of band gap [5]. Further radiation exposure/doping may result in formation of free radicals/changes in Pi-conjugated systems will also result in decrease of band gap [6]. Doping is also resulted in band shifts and decrease of band gap [7]. The authors have observed an optical absorption band for prestine PPy around 380–400 nm corresponding to Pi–Pi* transition; which shifted to 450–500 nm attributed to bi-polarans, with an additional band around 1200 nm corresponding to polarans. Similarly in Low pressure dependence of optical spectra of PAC and PPy: Electronic synthesis of PPy films doped with iodine–plasma [8] have observed intrinsic band of Pi–Pi* transition in 350–400 nm range but iodine doping resulted in suppression of this band and creation of new band at 400 nn (3.0 eV) 450–600 nm (2.5 eV–3.2 eV) and 1.0 eV. Therefore, the results confirm our observations. This analogy can be applicable sulfate doped PPy also as sulfate ions also cause disturbing of conjugated structure as well as chemical structure change of PPy.

FOURIER TRANSFORM INFRA-RED STUDIES

FTIR Spectrum of pristine PPy is as shown in as curve 2 in Figure 4; while curve 1 is spectrum of pristine PPy. The spectrum showed different absorption bands consequent to the chemical structure of polymer as given in Table 3. pristine PPy has shown characteristic absorption bands of 3400–3340 cm^{-1} (N–H stretch Vibration of pyrrole), 1620–1630 cm^{-1} (C=C/C–C vibrations of pyrrole group), 1530–1560 cm^{-1} (intra C=C ring/C–C inter-ring vibration) 1458–1480 cm^{-1} (C–N stretch Vibration), 1206–1293 (N–C stretch/=C–H plane vi in Polaran bands), 1147–1155 cm^{-1} (=–C–H in plane & out of plane Vib), 1020–1045 cm^{-1} (=–C–H in plane deformations), 910–925 (C–H out of plane bend/bipolaran oxidized state) and 750–780 cm^{-1} (C–H out of plane) [9–11].

Gamma irradiation of PPy results in following changes of FTIR bands [12–15]:

1. The Intensity and broadening of 3400–3500 cm^{-1} band reflects decrease of hydrogen bonding or crosslinking/decease in N–H vibration frequency.
2. Intensity variation of 1600–1700 cm^{-1} absorption band (C=N imine group) suggesting breakdown of pyrrole ring to form conjugated structures.
3. C=C, asymmetry strong of pyrrole ring vibration at 1540–1560 cm^{-1} appeared with decreased intensity.

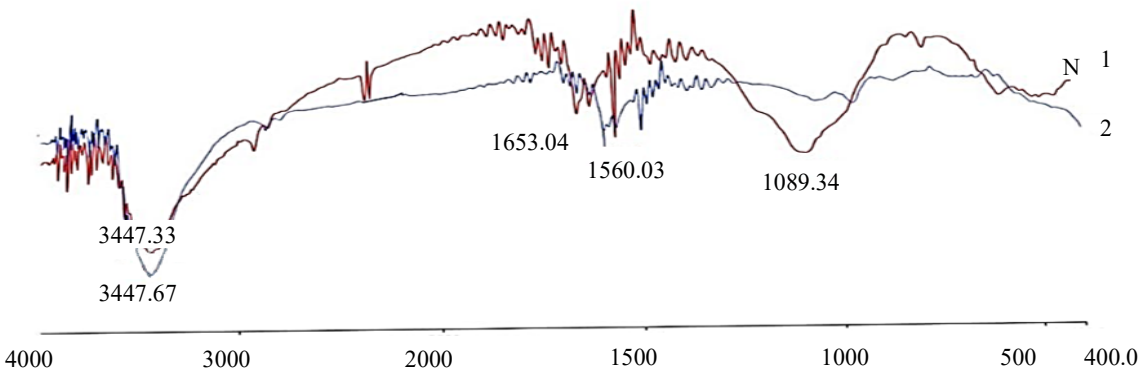

Figure 4. FTIR spectra of PPY Curve 1: Gamma irradiated: Curve 2: Pristine.

Effect of Doping on FTIR Bands

Different doping of FTIR spectra of PPy is shown in Figure 5.

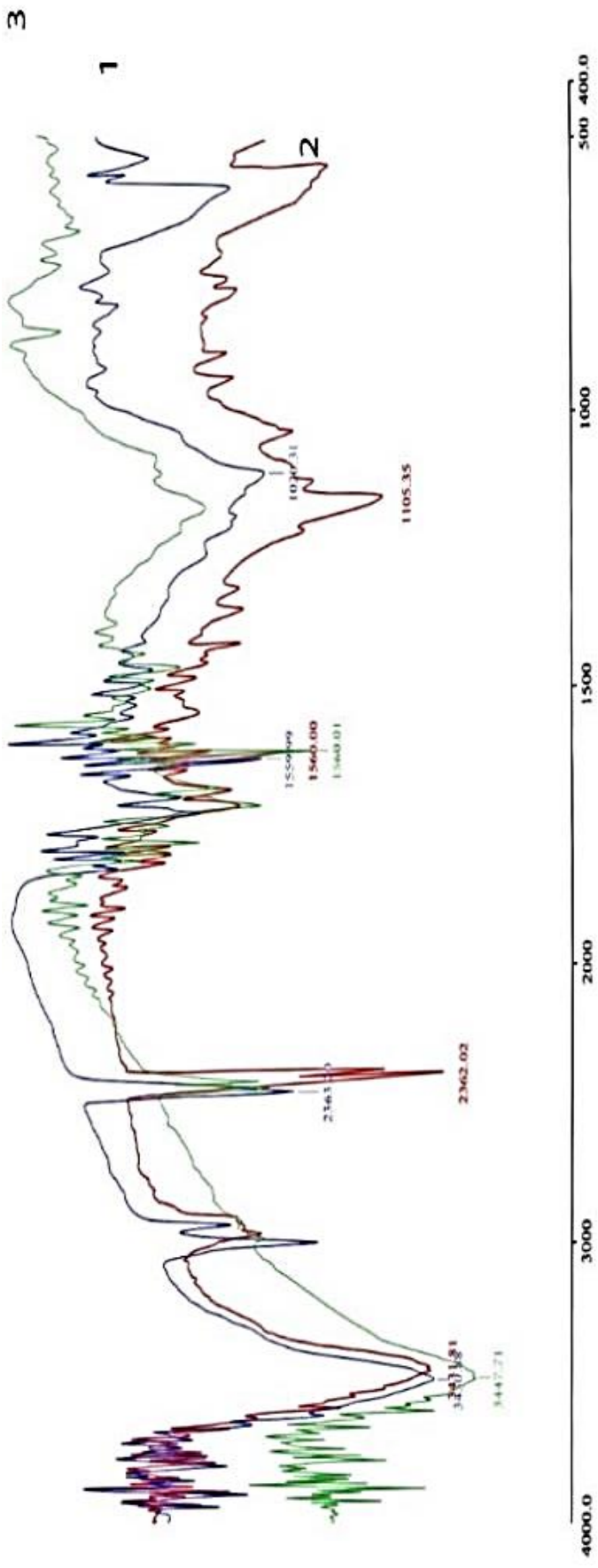

Figure 5. Comparison in FTIR spectra of PPy; Curve 1 sulfate doped; Curve 2 Bromine doped; Curve 3 Iodine doped.

Bromine Doping

Doping of bromine causes the following changes (1–3):

1. Broadening/weakening of 3400–3100 cm^{-1} band is indicative of the interaction of N–H groups with bromine creating/enhancing charged species like Polarans.
2. Variations in band positions/intensities of C=C/C–C intra-ring vibrations (1560–1520 cm^{-1}) C–N stretching vibrations of conjugated pyrrole ring at 1490–1450 cm^{-1}. This results modification of Pi electronic conjugated networks along back bone of polymer.
3. Increase/decrease and base line shifts of absorption bands [16–19].

Iodine Doping

Upon doping of iodine the absorption bands in the following regions were reported (1–3):

1. The N–H band at 3400–3100 cm^{-1} is expected to become broad or diminish depending on doping level.
2. The absorption band corresponding to intra ring C=C/inter ring C–C vibrations are expected to change due to doping
3. The major changes are expected Pyrrole ring–iodine reactions reflected by position and intensity variations of 1536, 1239 and 1043 cm^{-1} absorption band.

Sulfate Ions Doping

Doping of Sulfate ion is expected bring following changes in FTIR spectra [20–23].

The following changes are expected to occur:

1. The N–H vibrations of pyrrole ring are expected in 3400–3100 cm^{-1}.
2. Strong peaks in the region of 1640–1630 cm^{-1} are due to C=C backbone & intra ring vibrations.
3. 1480–1440 cm^{-1} band is due to C–N/C=C strong vibrations of pyrrole ring.
4. The C–H in-plane & deformation vibrations, C–N vibrations give band at 1315–1285 cm^{-1}.
5. N–C Strong Vibrations & C–H in-plane vibrational bands at 1180–1120 cm^{-1} region.
6. 1040–1020 cm^{-1} indicate the in-plane/deformations of pyrrole ring or presence of dopant.

Particularly the Sulfate doped PPy must show:

1. The band corresponding to S=O asymmetric String, which is an indication for successful doping and compensation of +ve charge in polymer chain.
2. 1100–1050 cm^{-1} is the additional stretching vibration of S=O groups.
3. 620–610 cm^{-1} band is due to SO_{-2} groups.

Table 3. Comparison FTIR band positions of PPy under different conditions.

Pristine Ppy	Gamma irradiated PPy	Sulphate doped PPy	Bromine doped PPy	Iodine doped PPy	Assignment
3400–3500	3904–3567	3447–3904	3904–3447	3904–3447	N–H Vibration.
2920	2926	2926	2910	2926	C–H of CH_2/CH_3
2300	2343, 2367	2343 2346	2346, 2351	2346, 2361	–N(+)=C–
1600–1700	1720	1688, 1720, 1735	1688, 1720, 1735	1655, 1720, 1736	C=O
1650	1622, 1655	1655	1655	1623	Conjugated groups.
1540–1560	1527, 1544, 1559	1523, 1544, 1560	1527, 1544, 1527	1527, 1544, 1580	C = C/ Aromatic N–H.
1450 – 1490		1467, 1344	1401	1464	C–N str Vib.
1200–1300		1105	1119	1089	C–N Str/=C–H plane vibrations/C–H out of plane vibrations.
1030–1050	1020				=C–H in-plane deformation.

CYCLIC VOLTAMETER

Cyclic voltometric pattern of PPy with different sweep voltages are as shown in Figure 6. The curves exhibit two different peaks corresponding to oxidation (0.25V) and reduction (0.75 V). The result suggests the conducting nature of polymer and agree with literature reports [24]. For a sweeping voltage of 100 mV/sec, the difference between oxidation and reduction potentials (Δ V OR) is 0.65 mV. With the decrease in sweeping voltage, the delta V OR gradually decreased and for sweeping voltage of 30 mV/sec, the Δ V OR decreased to 0.45 mV. Regarding anode current changes, the values change from 160 mA to 45 mA upon increase of sweep voltage change of 100 mV to 30 mV voltage sweep.

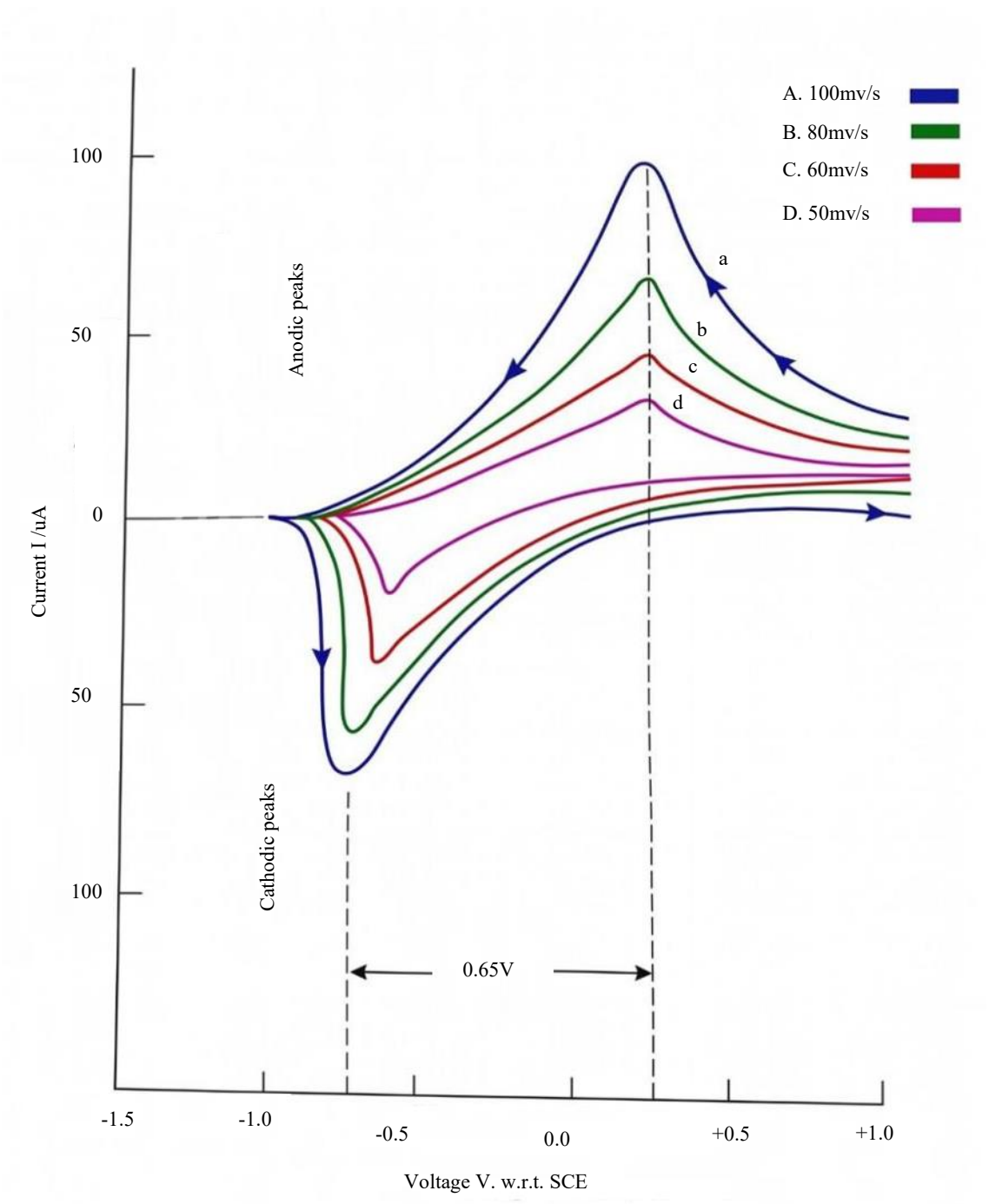

Figure 6. Cyclic Voltagrams of PPy with different sweeping voltages.

CONCLUSION

In conclusion, gamma-irradiation and doping successfully alter chemical and optical properties of polypyrrole (PPy). The optical absorption spectra of pristine PPy exhibited three absorption bands at 380 nm, 450 nm and 525 nm positions. They are assigned to Pi–Pi* transition, Bipolaran and Polarans present in PPy. Doping and gamma irradiation induce band shifts/intensity variations. The changes are explained. Using optical data, the band gap (Eg) and refractive index (n) values are measured. Variations in the Eg values and n values confirm the influence of irradiation and doping. FTIR spectra of PPy under different conditions approve chemical structure of the polymer and influence of gamma-irradiation and doping. The change in chemical structure and optical properties is assumed to be associated with oxidation and reduction processes in PPy. Cyclic–voltammetry results support this.

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