ISSN 2229-5518

Effects Of Gamma Irradiation On The Electrical And Optical Properties Of Conducting Poly(N-Methylaniline)

K. Gangadevi [1], S. Rajakarthihan [1], T. Mathavan [2,*], N.Rubiya Evangelin [2], J. Archana [3], M. A. Jothirajan [4], S. Umapathy [5]

[1] Department of Physics, Thiagarajar College, Madurai-625009, Tamilnadu, India
[2] Department of Physics, N.M.S.S.Vellaichamy Nadar College, Nagamalai, Madurai-625019, Tamilnadu, India
[3] Research Institute of Engineering, Shizuoka University, Japan
[4] Department of Physics, Arul Anandar College, Karumathur, Madurai-625514, Tamilnadu, India
[4] School of Physics, Madurai Kamaraj University, Madurai-625021, Tamilnadu, India
[*] Email: tjmathavan@yahoo.co.in

Abstract— The effects of gamma irradiation on the electrical and optical properties of conducting Poly(N-Methylaniline) have been studied. The radiations absorbed by the samples were 21.5KGy. The deterioration of chemical bonding with irradiation fluence was found. The conductivity measurement was carried out by using four-probe method in the temperature range 310 K - 370 K. The analysis of conductivity studies shows that the protonation increases in the order 1 M > 0.6 M > 0.4 M > 0.2 M of H_2SO_4 and the enhanced conductivity of samples due to irradiation. Arrhenius fitting of conductivity curves indicates that the charge transport mechanism was followed by VRH. The SEM images confirmed the morphological changes due to the gamma irradiation.

Index Terms— Minimum 7 keywords are mandatory, Keywords should closely reflect the topic and should optimally characterize the paper. Use about four key words or phrases in alphabetical order, separated by commas.

1 INTRODUCTION

Demand for polymers having enhanced properties is continuously on the rise due to their use for various scientific and technological applications [1], [2] . Irradiation of polymers has established itself as one of the most acceptable approach to alter polymer properties significantly " [3] " . Irradiation of polymers destroys the initial structure by way of cross linking, free radical formation, irreversible bond cleavages etc. that results in the fragmentation of molecules and formation of saturated and unsaturated groups. All of these processes introduce defects inside the material that are responsible for change in the optical and structural properties of the polymer [3].

2 EXPERIMENTAL

2.1 Materials and Methods

All chemicals used were of analytical reagent (AR) grade. PNMeA was synthesized by chemical oxidation of N-methylaniline (C_7H_9N) with ammonium peroxodisulfate (APS) ($(NH_4)_2S_2O_8$). The synthesized PNMeA was named as (PA-1). The PNMeA samples were mixed with different molar concentration of sulphuric acid (0.2 M, 0.4 M, 0.6 M, 0.8 M, 1M). The samples were named as PA-2, PA-3, PA-4, PA-5, PA-6. The mixtures were filtered and dried. Then the dried samples were irradiated using gamma ray source and are named as PAI-1, PAI-2, PAI-3, PAI-4, PAI-4, PAI-5, PAI-6. The radiations absorbed by the samples were 21.5KGy. The FTIR spectra were recorded using KBr pellets in the range of 4000 – 400 cm^{-1}. The UV–Vis spectra of the samples in N-Methyl-2- pyrrolidone (NMP) were recorded in the range of 200–900 nm. The temperature dependent dc resistivity measurements were carried out for samples using four probe method in the temperature range 310 K – 370 K. The temperature dependent conductivity data can be fitted to Arrhenius equation $\sigma = \sigma_0$ exp [-Ea/K_BT], where E_a is the activation energy, K_B is the Boltzmann constant and T is the temperature.

3 RESULTS AND DISCUSSION

3.1 DC Conductivity Measurements

The conductivity measurements were carried out in steps of 2 K using four probe set-up in the temperature range 310 K – 370 K. The conductivity values calculated from the graphs were listed in the Table 1. The increase in the DC conductivity can be considered as a result of the chain scission of the macromolecules induced by gamma irradiation [4]. This will in turn increases the molecular mobility.

ISSN 2229-5518

TABLE 1

CONDUCTIVITY VALUES OF THE SAMPLES BEFORE AND AFTER IRRADIATION

PN Me A samples	Conductivity in(S.Cm-1)	PN Me A samples	Conductivity in(S.Cm-1)
PA-1	-	PAI-1	0.434
PA-2	-	PAI-2	7.806
PA-3	0.104	PAI-3	10.706
PA-4	0.216	PAI-4	13.442
PA-5	0.307	PAI-5	15.562
PA-6	0.377	PAI-6	30.623

3.2 FTIR Spectral Analysis

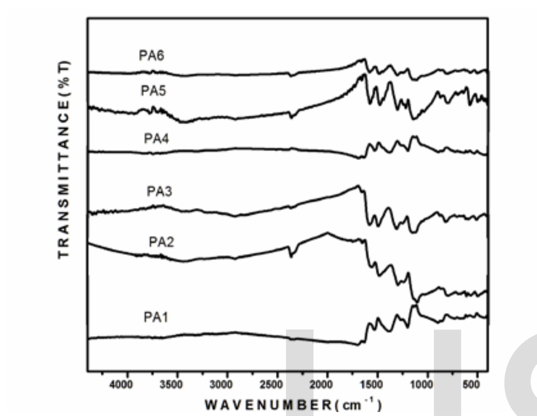


Fig.1. FTIR Spectra of the samples before Irradiation.

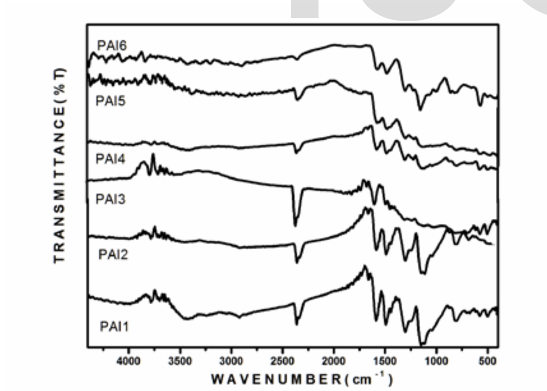


Fig.2. FTIR Spectra of the samples after Irradiation.

Fig 1 and 2 shows the FTIR spectra of synthesized pnmea and H_2SO_4 doped pnmea samples in the range 4000 – 400cm^{-1} before and after irradiation. These spectra are in. These spectra are in agreement with ones that already have been reported [4-6].

Infact, all poly (N-Methylaniline) presents similar FT-IR spectral patterns. In the spectra of pure pnmea is shown in fig. The ring stretch of quinoid forms is observed at 1593 Cm^{-1} and benzoid forms are absorped at 1500 Cm^{-1}. Also the band at 1379 Cm^{-1} is associated with CH_3N group, while the band at 1310 Cm^{-1} can be attributed to the imine group. The absorption peak at 1147 Cm^{-1} is characteristic of the electron- like absorption of N=Q=N vibration that Q denotes the quinoid ring. The band at 830 Cm^{-1} corresponds to C-H bending vibrations of the p-substituted benzene ring. This later observation confirms the expected head-to-tail coupling polymerization PNMEA at the C-4 and N positions. Similarly the spectral data for various concentrations of the sample before and after irradiation were recorded.

3.3 UV – VIS SPECTRAL ANALYSIS

Fig 3 and 4 shows change in optical spectra accompanying doping are significant and these spectral changes play a key role in elucidating the mechanism of doping and the nature of charge storage species in the polymer chain UV-Vis spectrum of emeraldine base in n-methylpyrrolidinone (NMP) solution, shows two electronic transitions at 325 nm (3.9 eV) and 635 nm (2 eV).

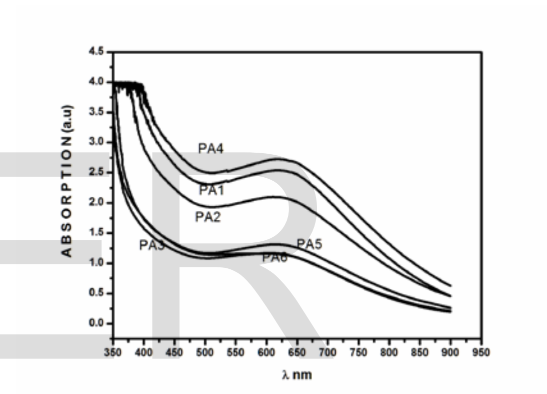


Fig.3. UV – Vis Spectra of the samples before Irradiation.

For instance, PNMeA exhibits an intense π-π* transition. The band at 325nm is related to polaron transition and the band at 635 nm related to bipolaron transition [7], [8] . In these spectra the localized polaron band shifts to higher wavelength from methyl to butyl substitution, respectively.

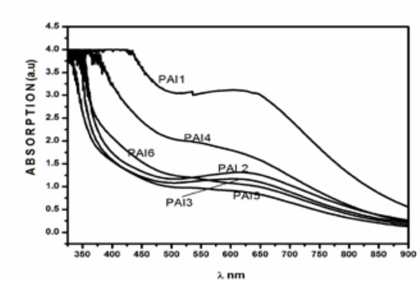
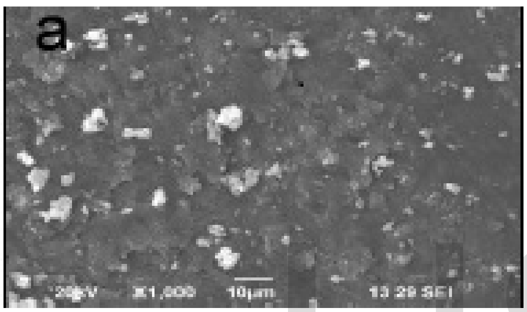


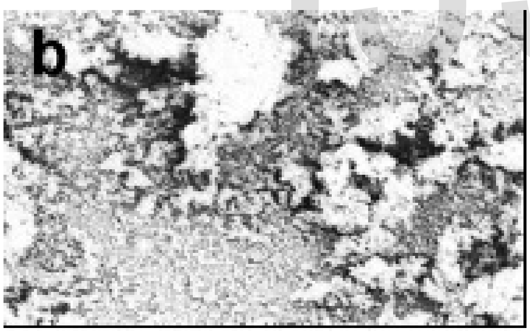
Fig.4. UV – Vis Spectra of the samples after Irradiation.

3.4 Scanning Electron Microscopy

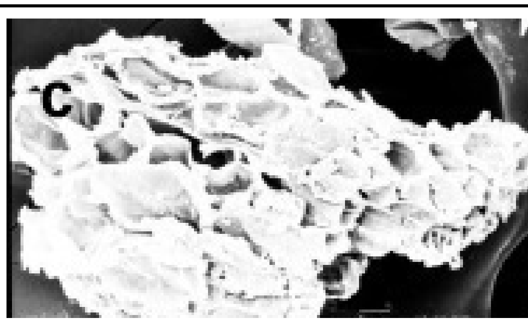
The SEM images shows that the surface morphology of the samples before and after irradiation. The variation in microstructure leads to different conductivity of the sample. The conductivity depends on the structure. Before irradiation the samples PA1 and PA2 have irregular structure. For the samples PA3 to PA6, the SEM image shows the globular structure due to the high molar concentration. In the unirradiated sample shows lesser amount of conductivity due to the disorderness of the polymer. The large and uniform fibrillar structure formed due to the gamma radiation on the sample. The change in the morphology after irradiation produces the microstructural variation which enhanced the conductivity of the sample further more. It is noticed that even a small variation in the in the microstructure will leads to the enourmous change in the conductivity which is confirmed by the tubular structure of the sample PAI-6 due to gamma irradiation.



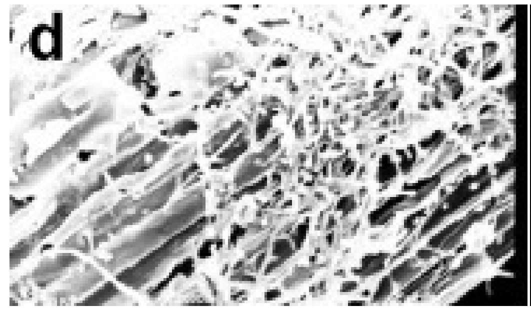
(a)SEM images of the sample PA1



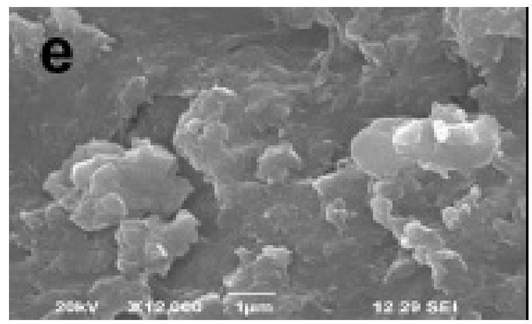
(b)SEM images of the sample PA2



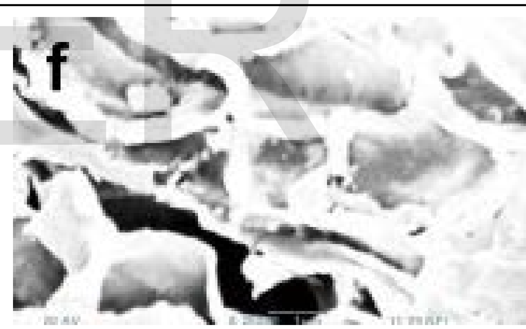
(c)SEM images of the sample PA3



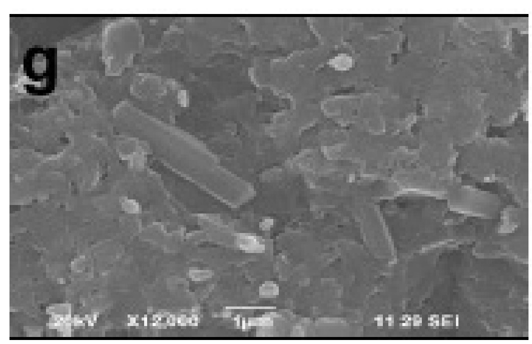
(d)SEM images of the sample PA4



(e)SEM images of the sample PA5

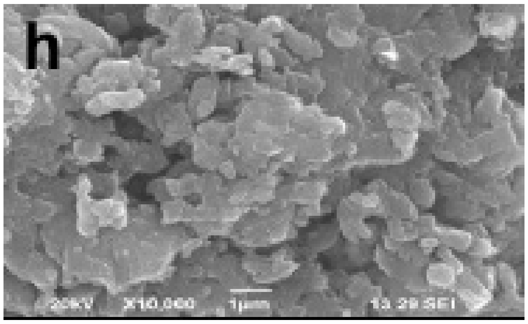


(f)SEM images of the sample PA6

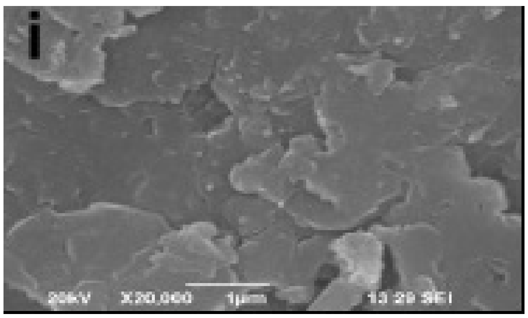


(g)SEM images of the sample PAI1

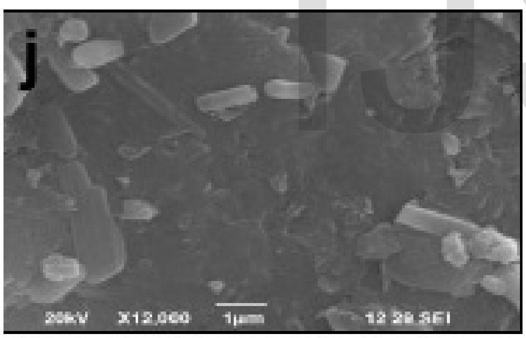
ISSN 2229-5518



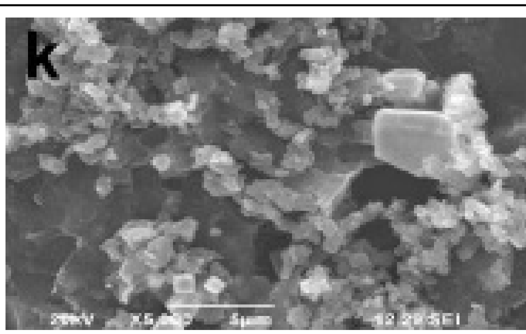
(h)SEM images of the sample PAI2



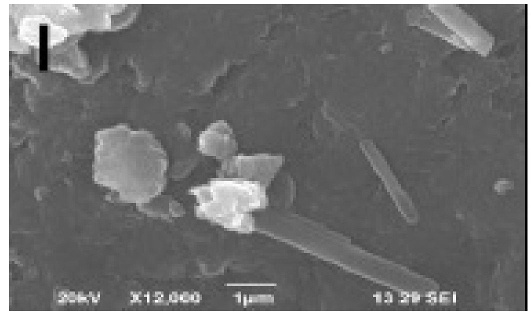
(i)SEM images of the sample PAI3



(j)SEM images of the sample PAI4



(k)SEM images of the sample PAI5



(l)SEM images of the sample PAI6

4 Conclusion

The effects of gamma irradiation on the electrical and optical properties of conducting Poly(N-Methylaniline) have been studied. The radiations absorbed by the samples were 21.5KGy. The deterioration of chemical bonding with irradiation fluence was found. The conductivity measurement was carried out by using four-probe method in the temperature range 310 K - 370 K. The analysis of conductivity studies shows that the protonation increases in the order 1 M > 0.6 M > 0.4 M > 0.2 M of H_2SO_4 and the enhanced conductivity of samples due to irradiation. Arrhenius fitting of conductivity curves indicates that the charge transport mechanism was followed by VRH. The SEM images confirmed the morphological changes due to the gamma irradiation.

Acknowledgment

One of the author T.Mathavan, thank the management of NMSSVN College to carry out this work.

References

[1] R. Mishra, S. Tripathy, D. Sinha, et al. Optical and electrical properties of some electron and proton irradiated polymer. *Nucl Inst and Meth B*. 2000, 168, 59.
[2] R. Mishra, S. Tripathy, K. Drivedi, et al. Effect of electron irradiation on polytetrafluoro ethylene. *Radiat Meas*. 2003, 37, 247.
[3] M. Nasef, M. Dahlan, M. Khairal. Electron irradiation effects on partiallyfluorinated polymer films: Structure-property relationships. *Nucl Inst and Meth B*. 2003, 201, 604.
[4] J. Tang, X. Jing, B. Wang & F. Wang, Synth Met, 24, 1988, 231.
[5] S. K. Manohar and G. MacDiarmid, Synth Met, 29, 1989, 349.
[6] A. A. Athawale , B. Deore , M. Vedpathak and S. K. Kulkarni , J Appl Polym Sci, 74, 1999, 286.
[7] D. Bansi Malhotra , Handbook of polymers in electronics, (Rapra technology limited ,UK) 6, 2002.
[8] D. Bloor and B. Movagher., IEEE proceedings.130(5), 225 (1983).