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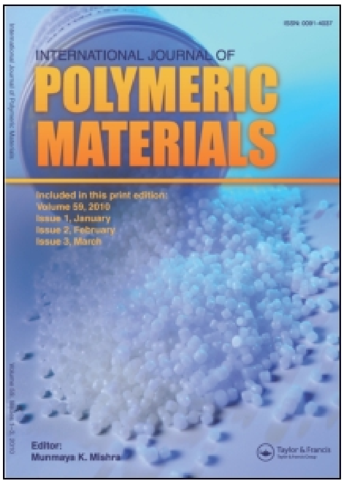

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Effects of Si^{5+} Ion Irradiation on Poly(3-methyl thiophene) Films

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Effects of Si^{5+} Ion Irradiation on Poly(3-methyl thiophene) Films

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Poly(3-methyl thiophene) has been synthesized by the chemical oxidation polymerization method using $FeCl_3$. The powder has been dissolved in $CHCl_3$ and thin films of thickness 2 μm are prepared on glass and Si substrates. The polymerization has been confirmed by FTIR spectrum. The films are irradiated by 60 MeV Si^{5+} ions at different fluences and modifications in optical, electrical and structural properties are studied. FTIR spectra show methyl group evolution after irradiation. The optical band gap decreases after irradiation and dc conductivity increases four orders of magnitude after irradiation at the highest fluence. The conduction mechanism has been found mainly by band conduction.

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Keywords dc conductivity, FTIR and XRD, optical band gap, poly(3-methyl thiophene)

INTRODUCTION

Polythiophene and most of its derivatives polymerized by electrochemical polymerization are insoluble in almost all solvents. However, poly(3-alkylthiophenes) synthesized by chemical method can be soluble under certain

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conditions [1]. In the undoped state, the majority of polymers of polythiophene series possess a red or orange tint, while at the high doping degrees they acquire a blue–green color. This property is characteristic of such polymers as polybithiophene, poly-3-methylthiophene, poly-3-hexylthiophene [2], poly-3-octylthiophene [3], polyisothionaphthene [4,5], and many others. Most electrically conducting polymers are insoluble in their doped states [6]. A strategy of affording to dissolve conducting polymers is to introduce a functional group with solvent affinity to a monomer or a polymer backbone. The introduction of long alkane chains to a thiophene ring makes it possible to dissolve the polythiophene in organic solvents [7,8].

Poly(3-alkylthiophenes) have been found to be an unusual class of polymers with good solubility, processibility, environmental stability, electroactivity, and other interesting properties. Polythiophenes with suitable substituents in 3-position not only will have better processibility and stability, but may also possess novel electrical, electrochemical and optical properties [9,10]. Moreover, the presence of substituents in 3-position can even lead to novel physical phenomena that are not found in the unsubstituted parent form. Therefore, the synthesis of 3-substituted polythiophenes has attracted much interest both from synthetic considerations as well as from material science.

Although electrochemical polymerization is suitable for the preparation of poly (3-methyl thiophene) (P3MT), the polymers are not processible when these are formed. In addition, the yield of the polymers is low and the polymers often do not have a well-defined structure [11]. Chemical oxidative polymerization is found to be suitable for the polymerization of polythiophene and P3MT with iron(III) chloride ($FeCl_3$) because it produces the processible polymers in high yield [11].

SHI irradiation induces interesting changes in polymer properties by changing its structural properties. An increase in hardness, strength, and wear resistance [12–14], electrical conductivity [15–17], density [16], chain length [12–17], crystallinity [13–16], solubility [12–15], and improvements in the optical transmission [14–17] properties of the polymers have been reported. These changes depend upon the sample parameters like composition, molecular weight, and temperature, and ion beam parameters such as energy, mass, and fluence. 120 MeV Si^{9+} ion irradiation effects on electropolymerized P3MT have been studied [18] and it was found that the conductivity and crystallinity of the polymer increases after irradiation.

In the present study, poly(3-methyl thiophene) (P3Mt) powder has been prepared by chemical oxidation polymerization method. The powder has been dissolved in chloroform. Dip-coated films have been prepared on glass and silicon substrates. The films have been irradiated with 60 MeV Si^{5+} ions at different fluencies as 3.3×10^{10}, 10^{11}, 3.3×10^{11}, 10^{12}, and 3.3×10^{12} ions/cm^2. Pre- and post-irradiation XRD, UV-visible absorption, FTIR and dc conductivity studies have been carried out to study the effects of irradiation.

Experimental

The monomer 3-methyl thiophene (99.9%), chloroform (AR grade), anhydrous $FeCl_3$, EDTA and ethyl alcohol were procured from Alfa-Aesar Company. The polymer powder has been prepared by chemical oxidation polymerization method [19] and washed thoroughly with EDTA and ethyl alcohol to remove Fe content and nonpolymerized contents. The undoped powder so obtained was dissolved in chloroform to prepare thin films of thickness 2 μm by dip-coating method on glass and Si substrates.

Samples have been irradiated by 60 MeV Si^{5+} ions generated from the 15 MV Pelletron Accelerator at the Inter University Accelerator Center, New Delhi. Calculating the range using TRIM code, the thickness of the samples were chosen such that the energy range is larger than the film thickness. Irradiations were carried out at different fluences like 1×10^{11}, 3.3×10^{11}, 1×10^{12}, 3.3×10^{12}, and 1×10^{13} ions/cm^2.

In order to obtain information about crystallinity, XRD studies were carried out using a Bruker AXS, D-8 Advance X-ray diffractometer, on pristine and irradiated samples. In order to obtain information about the optical properties of these films, FTIR and UV-visible spectroscopy have been carried out on the blended films using a Nexus-670 FTIR spectrometer and Camspec M-550 double-beam scanning UV-visible spectrophotometer. The dc conductivity of both irradiated and pristine polymers was measured by using the two-probe method in the temperature range 300–400 K using a specially designed metallic sample holder. These measurements were made at a pressure of about 10^{-3} Torr. A voltage of 2 V was applied through regulated power supply and the resultant current was measured with a Pico ammeter to measure the dc conductivity within 1% accuracy [25].

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X-Ray Diffraction Studies

The X-ray diffraction (XRD) patterns of unirradiated and irradiated poly(3-methyl thiophene) films have been given in Figure 1. It is clear from the figure that the synthesized polymer is semicrystalline in nature. After irradiation at highest fluence a new peak appears at 32° which shows an increase in crystallinity of the polymer. The crystallinity of P3Mt is less when compared to other conducting polymers. This is due to the presence of a methyl group attached to the thiophene ring, which provides steric hindrance to the linear arrangement of the polymer chains. Upon SHI irradiation, collective excitations are produced which in turn produce a large excited volume. In this the backbone bonds may rotate and adopt a variety of conformations. As they cool, the lower energy positions will be preferred. The steric hindrance will become less effective due to the decrease in methyl groups after irradiation which may cause the decrease in the amorphous nature.

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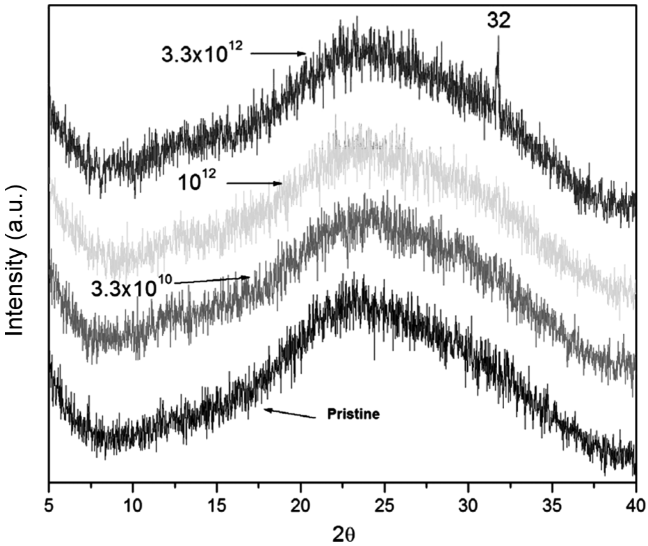

Figure 1: XRD spectra of pristine and irradiated P3Mt films.

FTIR Studies

The FTIR absorption spectra of pre- and post-irradiated poly(3-methyl thiophene) films prepared on Si substrate are shown in Figure 2. The peak at $625\,\mathrm{cm}^{-1}$ represents the C–S stretching vibration peak of poly(3-methyl

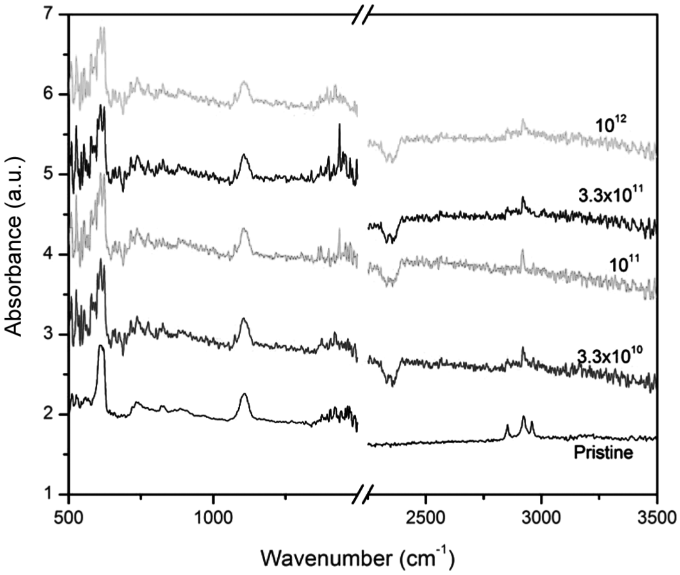

Figure 2: FTIR absorption spectra of pristine and irradiated P3Mt films on Si substrates.

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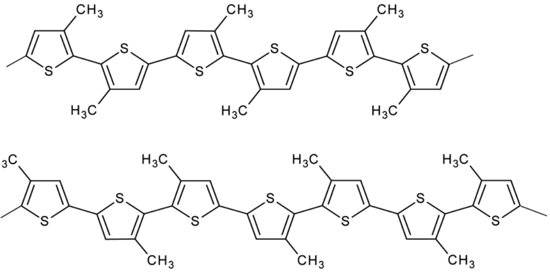
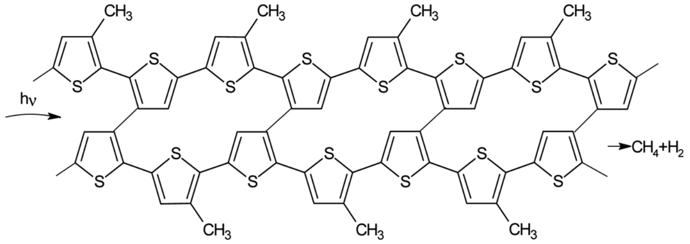
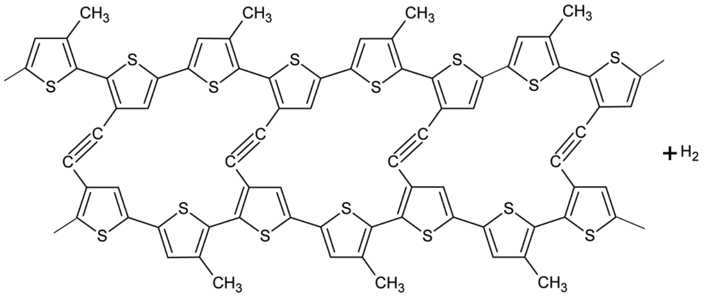
thiophene). The peak at 730 cm^{-1} is attributed to the C–S stretch of sulphides. The peak at 830 cm^{-1} is due to the C–H ring vibration of thiophene. The C–H in-plane vibration occurs at 1105 cm^{-1}. The peaks at 2850 and 2920 cm^{-1} are attributed to asymmetric and symmetric stretching vibration of the methyl group. The =C–H stretching vibration occurs at 2960 cm^{-1}. From this the formation of poly(3-methyl thiophene) is confirmed. After irradiation the peaks



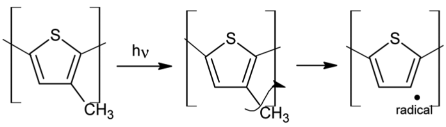
Chemical structure: poly(3-methyl thiophene)



Possible mechanism of crosslinking in poly(3-methyl thiophene) due to radiation



Possible triple bond formation



Radical formation

Scheme 1: Bond formation mechanism due to ion irradiation.

at 2850 and 2960 cm^{-1} vanish and a very less intense peak at 2920 cm^{-1} remains. This shows the evolution of the methyl group after irradiation. The C−H in-plane vibration stretch at 1100 cm^{-1} and the C−S stretching vibration at 625 cm^{-1} do not show much change, which implies the rings are not much destroyed due to irradiation. The other peaks at 730 and 830 cm^{-1} show a decrease in intensity. From this it is clear that the main change in the polymer is due to the release of the methyl group. The C≡C stretch appears in the irradiated samples at 2350 cm^{-1}. The possible mechanism of crosslinking, bond formation and radical formation has been given in Scheme 1.

UV-Visible Absorption Studies

The UV-visible absorption spectra of pristine and irradiated samples have been shown in Figure 3. The spectrum has two peaks at 290 nm and 410 nm. The peak at 290 nm has been attributed to n-π^* transition and the other peak at 410 nm is attributed to π-π^* transition. With an increase in fluence the π-π^* absorption intensity decreases. The optical band gap has been measured from Tauc's relation as given in reference [20–22]. The photon energy hν vs $(\alpha h\nu)^{1/2}$ has been plotted in Figure 4 to measure the change in the optical band gap after irradiation at difference fluences.

The optical band gap has been found to decrease after irradiation with an increase in fluence. The fluence versus optical band gap has been plotted in Figure 5. At low fluences the n-π^* transition intensity increases when compared with π-π^* transition intensity. At higher fluences both n-π^*, π-π^*

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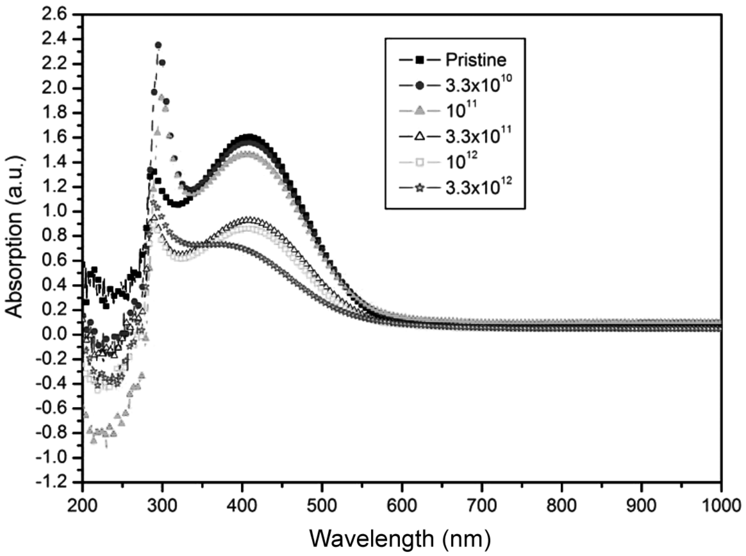

Figure 3: UV-visible absorption spectra of pristine and irradiated P3Mt films.

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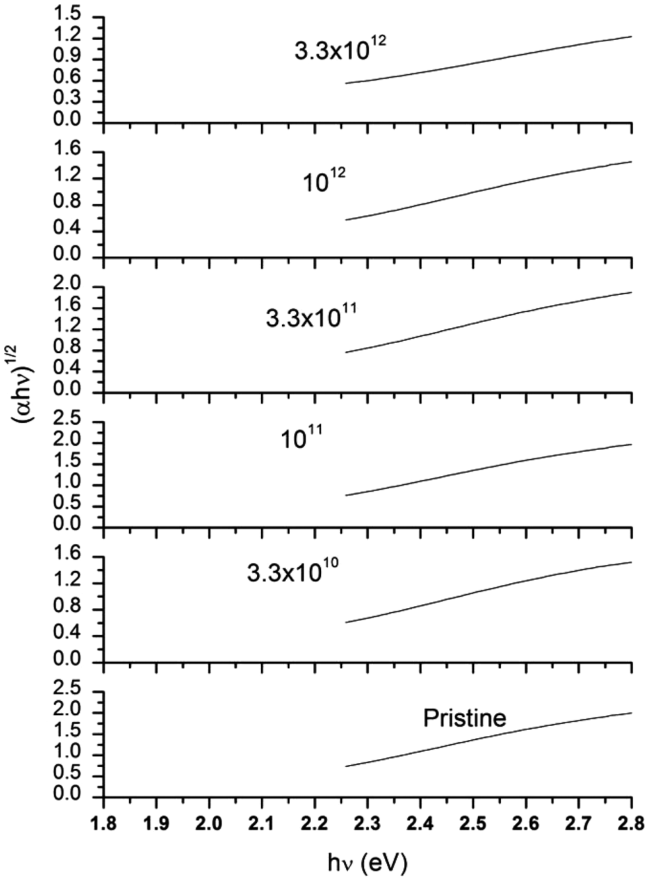

Figure 4: Photon energy vs. $(\alpha h\nu)^{1/2}$ at different fluences.

transition intensities decrease. The decrease in band gap may occur due to the broadening of polaron bands, which is attributed to the increase in carrier concentration in the polymer films as a large number of cations, anions, radicals and charged particles are created upon SHI irradiation. Triple bond formation also plays a role in the decrease in optical band gap.

DC Conductivity Studies

The dc conductivity measured from room temperature to 400 K and the Arrhenius plots of dc conductivity vs. temperature are given in figure 6. The dc conductivity at 320 K has been found to increase after irradiation. The conductivity increases exponentially with temperature and also increases 4 orders of magnitude after irradiation. Fluence vs. dc conductivity and activation energy (ΔE) have been plotted in Figure 7. From Figure 7 it is

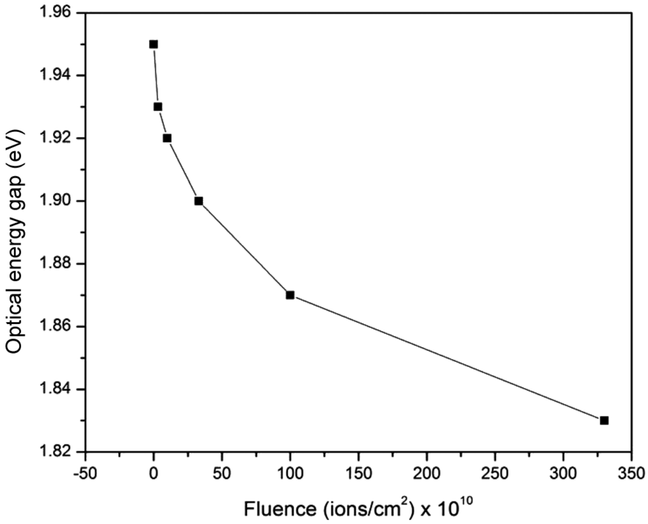

Figure 5: Fluence vs. optical band gap.

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clear that the dc conductivity increases with fluence and activation energy decreases. Different models for conduction mechanism in conjugated polymers were proposed [23–26]. In the present case the dc conductivity obeys the relation

$$\sigma = \sigma_0 \exp(-E_A/k_B T)$$

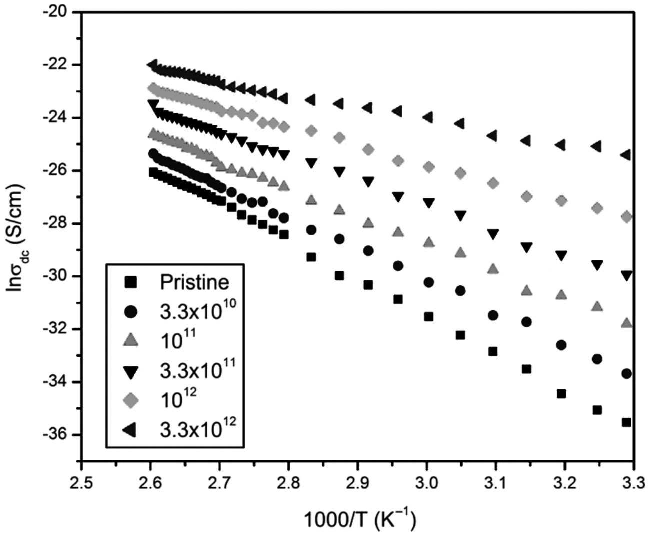

Figure 6: Arrhenius plots of dc conductivity of pristine and irradiated P3Mt films.

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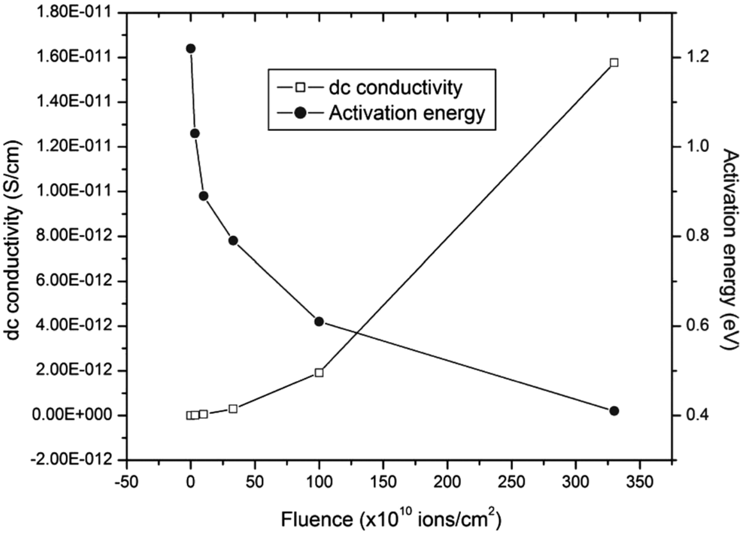

Figure 7: Fluence vs. dc conductivity at 320 K and activation energy.

where, E_A is the activation energy. Therefore the conduction is predominantly brought about by thermally excited free charge carriers and the mechanism of conduction may be due to band conduction. The concentration of thermally activated carriers increases with fluence. The values of dc conductivity (σ_{dc}), pre-exponential factor (σ_0) and activation energy (ΔE) are tabulated in Table 1.

During irradiation the release of various gases takes place which leads to the formation of carbon-rich clusters along the path of the beam. As the fluence increases these paths overlap and may cause an increase in the crystallinity of the polymer, which in turn causes the increase in the conductivity. The decrease in optical band gap shows an increase in carrier concentration after irradiation. After irradiation triple bond formation was observed from FTIR which causes the delocalization of charge carriers at the Fermi level, which causes an increase in the electrical conductivity.

Table 1: Values of σ_{dc}, σ_0, and activation energy at different fluences.

Fluence (ions/cm^2)	**Activation energy (ΔE) eV**	**σ_{dc} at 320 K (S/cm)**	**σ_0 at 320 K (S/cm)**
Pristine	1.22	2.80×10^{-15}	1.63×10^{-5}
3.3×10^{10}	1.03	1.67×10^{-14}	2.81×10^{-3}
10^{11}	0.89	5.26×10^{-14}	1.47×10^{-1}
3.3×10^{11}	0.79	2.93×10^{-13}	1.02
10^{12}	0.61	1.91×10^{-12}	1.12×10^2
3.3×10^{12}	0.41	1.58×10^{-11}	2.00×10^4

CONCLUSIONS

Poly(3-methyl thiophene) has been successfully prepared by chemical method. The polymerization has been confirmed from FTIR studies. The dc conductivity of pristine polymer was measured to be 10^{-15} S/cm. Irradiation induces interesting changes in poly(3-methyl thiophene). The dc conductivity increases 4 orders of magnitude after irradiation. The optical band gap and thermal activation energy were found to decrease after irradiation. The release of various gases including radiation sensitive methyl group during irradiation causes the crosslinking in poly (3-methyl thiophene). New crystalline peak appears at highest fluence showing the decrease in amorphous nature which causes the increase in conductivity of the polymer.

The conductivity was found mainly due to band conduction. The polymer becomes inhomogeneous after irradiation due to the release of various gases. The formation of carbon-rich cluster along the path of the ion beam is found to increase with fluence. This cluster formation makes the polymer inhomogeneous, which in turn favors the increase in band conduction. From UV-visible absorption spectra, the intensity of the π-π^* transition peak decreases after irradiation, showing the decrease in insulating nature.

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