

Effects of an Oxygen-ion Beam (O^{+7} , 100 MeV) and γ Irradiation on Polypyrrole Films

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ABSTRACT: Nanostructured polypyrrole films doped with *para*-toluene sulfonic acid were prepared by an electrochemical process, and a comparative study of the effects of swift heavy ions and γ -ray irradiation on the structural and optical properties of the polypyrrole was carried out. Oxygen-ion (energy = 100 MeV, charge state = +7) fluence varied from 1×10^{10} to 3×10^{12} ions/cm², and the γ dose varied from 6.8 to 67 Gy. The polymer films were characterized by X-ray diffraction, ultraviolet–visible spectroscopy, and scanning electron microscopy. The X-ray diffraction pattern showed that after irradiation, the crystallinity

improved with increasing fluence because of an increase in the crystalline regions dispersed in an amorphous phase. The ultraviolet–visible spectra showed a shift in the absorbance edge toward higher wavelengths, which indicated a significant decrease in the band gap of the polypyrrole film after irradiation. The scanning electron microscopy study showed a systematic change in the surface of the polymer. A similar pattern was observed with the γ irradiation. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2502–2507, 2010

Key words: polypyrroles; UV-vis spectroscopy; X-ray

INTRODUCTION

Nanotechnology is rapidly evolving to open new materials useful for solving challenging bioanalytical problems and improving stability and sensitivity. Conducting polymers are exploited as excellent tools for the preparation of nanocomposites with entrapped nanoscaled biomolecules. Some of the conducting polymers, modified by nanomaterials, exhibit unique catalytic¹ or affinity² properties that can be easily applied in the design of biosensors. During the past few years, there has been extensive development in smart materials, which have functionalities ranging from the medical sciences to engineering sciences. Many smart materials, including conducting polymers, have hence gained increasing importance.³ Several conducting polymers, such as polypyrrole (Ppy), polyaniline, and polythiophene, have found a variety of applications as electronic and optoelectronic devices.^{4,5} Electronic conducting polymers have attracted extensive interest in both fundamental and applied research. The technological

applications developed at present are the transport properties of these conducting polymers. In parallel with the development of stable conducting polymers, charge carrier transport in the metallic state in such polymers has been the subject of intensive research.⁶ Ppy is an especially promising inherently conducting polymer, as it is highly conducting, environmentally stable, and relatively easy to synthesize. It has recently found applications in a wide range of fields, including chemical and biological sensors,^{7,8} light-emitting diodes,⁹ electromagnetic interference shielding,¹⁰ and advanced battery systems.^{11,12} Because of their commercial uses, conducting polymers have become a subject of scientific and commercial interest. So the use of ion irradiation on these materials is of great importance for the modification of the properties of these materials. Any modification of a material depends on the structure and the ion beam parameters (ion mass energy and fluence) and the nature of target material itself. With the use of high-energy heavy ions, dramatic modifications in the materials have been observed, which have been attributed to the scissoring of polymer chains by incident ions, breaking of covalent bonds, crosslinking, formation of carbon clusters, liberation of volatile species, and in some cases, even the formation of new chemical bonds.^{13–16} A similar trend was found in the absorbance of polyaniline after irradiation by a 160-MeV Ni⁺¹²-ion beam.¹⁷ Some

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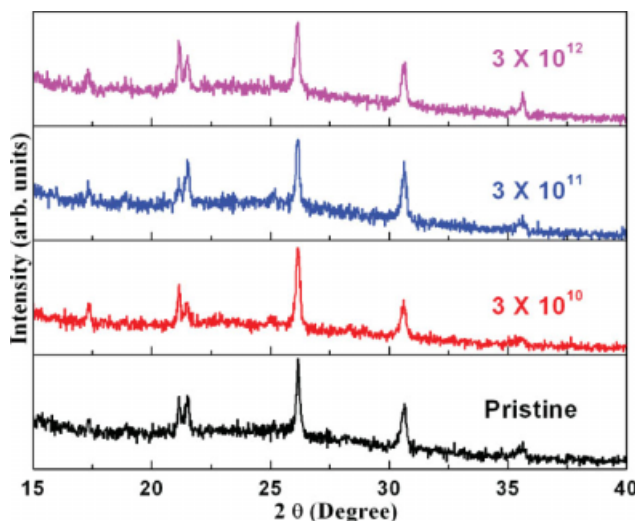


Figure 1 X-ray diffraction of the Ppy films irradiated by the O^{+7} -ion beam. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

other studies have also shown that the crystallinity of the Ppy films increased with irradiation with a sharp decrease at high fluences.¹⁸

EXPERIMENTAL

Polypyrrole films were prepared by the anodic oxidation of a pyrrole monomer. In the electrochemical polymerization of the pyrrole, indium tin oxide (ITO) and a platinum plate were used for the working and counter electrodes, respectively. The pyrrole monomer (Merck, India used as received) and *para*-toluene sulfonic acid (Lancaster, United Kingdom; >98%), both of which had a normality of 0.1M, were dissolved in distilled water. The platinum plate was used as a counter electrode, and the electrochemical polymerization of the pyrrole was carried out on ITO; during the polymerization, the anodic potential was kept at 0.8 V. The thickness of the thin films was controlled by variation of the deposition time. The thickness in this study was selected to be thin enough to allow the 100-MeV oxygen ions to completely pass through the film. Self-standing films of Ppy 1 cm² in size were irradiated in a material science beam line under high vacuum (5×10^{-6} torr) with 100-MeV oxygen ions with a beam current of 1 pA available from a 16-MV Pelltron tandem electrostatic accelerator (Inter University Accelerator Center, New Delhi, India) with various fluences ranging from 3×10^{10} to 3×10^{12} ions/cm². X-ray diffraction of the Ppy thin films were carried out with a Bruker AXS X-ray diffractometer with Cu K α radiation (1.54 Å) for a wide range of Bragg's angles (2θ ; $15 < 2\theta < 40$). Ultraviolet-visible (UV-vis) spectra were obtained with a U-3300 spectrophotometer (Hitachi, Japan). The ITO substrate was taken as ref-

erence during the measurements. Scanning electron microscopy (SEM) images were obtained with a Bruker AXS and a Zeiss EVO 40 EP scanning electron microscope.

RESULTS AND DISCUSSION

X-ray diffraction

The X-ray diffraction patterns of the pristine and oxygen-ion-irradiated nanostructured Ppy films are shown in Figures 1 and 2. The diffraction pattern revealed that the broad background decreased and the relative intensity of the characteristic peak at 26.25° increased with increasing ion fluence. The increase in the relative intensity of this peak signified the increase in the crystalline behavior with ion irradiation. The crystallinity of the polymers may have arisen because of the formation of single or multiple helices¹⁹ along their length or because of the crosslinking between polymer chains.¹⁷ Therefore, more crystalline regions would have been produced in the polymer film due to crosslinking between the polymer chains; this demonstrated the increase in the crystalline behavior of the polymer film after swift heavy ion (SHI) irradiation. The degree of crystallinity for the polymers (C) was calculated with the following relation:

$$C = \frac{A}{A'} \times 100\% \quad (1)$$

where A is the total area of the peaks (area of the crystalline and amorphous peaks) and A' is the total area under the diffractogram,¹⁷ that is, the total area from 5 to 40°. The crystallinity (%) calculated with this relation is shown in Table I.

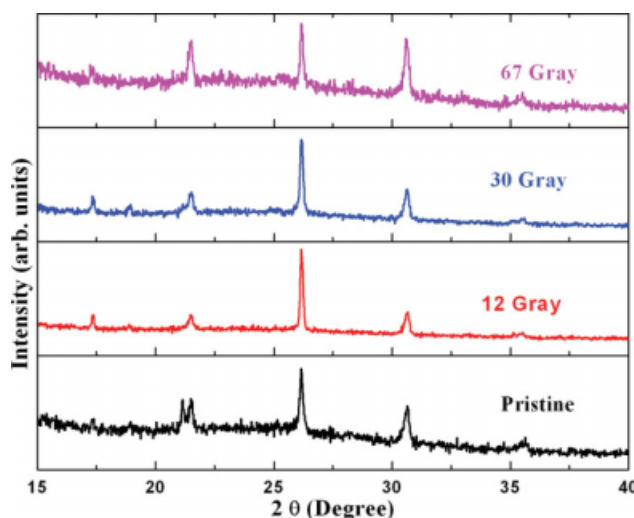


Figure 2 X-ray diffraction of the Ppy films exposed to γ rays. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Crystallinity Percentage of the Ppy Films

O ⁷⁺ -ion fluence (ions/cm ²)	Crystallinity of Ppy (%)	γ-ray dose (Gy)	Crystallinity of Ppy (%)
Pristine	23.02	Pristine	23.02
3 × 10 ¹⁰	26.91	6.8	23.45
3 × 10 ¹¹	30.39	12	23.90
1 × 10 ¹²	—	30	25.69
3 × 10 ¹²	32.21	68	26.60

UV-vis spectroscopy

The electronic structure and the carrier type in the polymers was visualized by UV-vis spectra. In this study, the absorption spectrum of Ppy exposed to different fluences of nickel beam was measured in the range 250–750 nm. The UV-vis spectra recorded for the Ppy films irradiated by an oxygen-ion beam and γ rays are shown in Figures 3 and 4. The electronic structure and the carrier type in the polymers could be visualized by UV-vis spectra. The energy band gaps of organic semiconductors have been the subject of many spectroelectrochemical studies,²⁰ which have identified polarons and bipolarons as charge carriers in conducting polymers. The absorption peak around 450 nm was the polaron absorption peak of the conducting Ppy,²¹ which was assigned to the transition between the valence and conduction bands across the band gap. The intensity of the absorption peak was found to increase, and a slight shift toward a higher wavelength was also found with increasing fluence. The intensity of the absorption was directly proportional to the quantity of carrier present in the polymer film. A shift in the

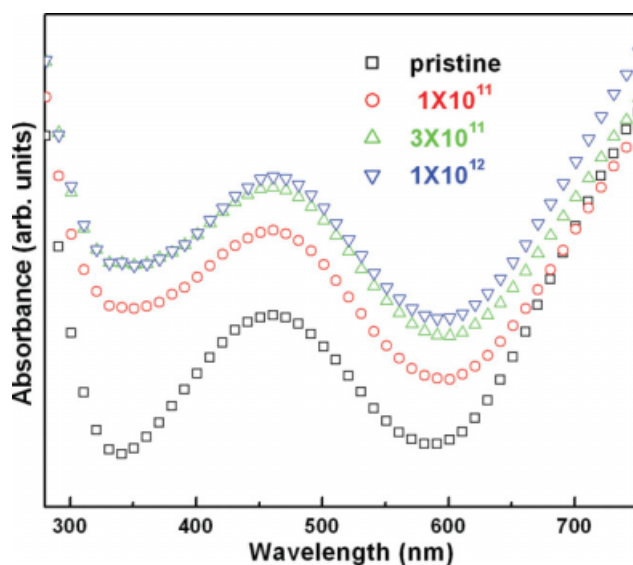


Figure 3 UV-vis of the Ppy films irradiated with the O⁷⁺-ion beam. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

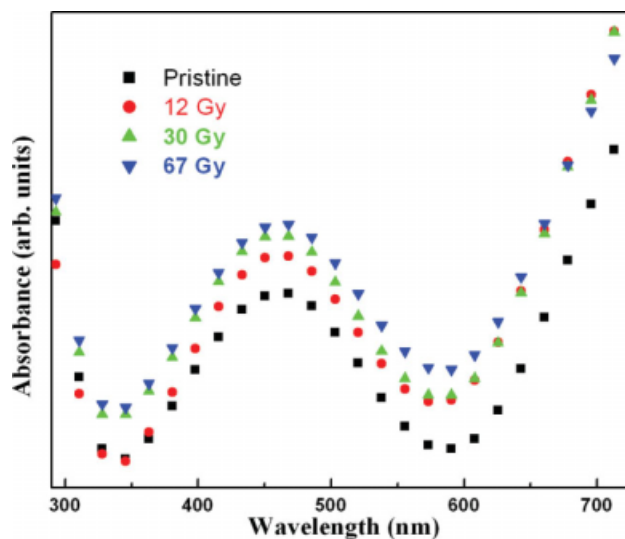


Figure 4 UV-vis of the Ppy films exposed to γ rays. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

absorption peak toward a higher wavelength indicated a decrease in the energy band gap of the polymer after SHI irradiation, which gave rise to an increase in the direct-current conductivity (Table II) of polymers. This shift in the absorption may have been produced in the creation of free radicals or ions and, thus, had the capability of increasing the conductivity of the polymers. This change was attributed to bond breaking and the formation of carbon clusters. The increased conjugation was attributed to the increased total energy deposited in the medium.

After γ-ray irradiation, the absorbance increased, but no shift was observed in the absorption peak. So there was no significant change in the energy band gap after γ-ray irradiation. This may have been because of a lower linear energy transfer of γ rays in the polymer. From the absorption, the band gap of the Ppy films was calculated by the linear part of Tauc's plot²² by the extrapolation of the plot of photon absorption $(\alpha h\nu)^2$ versus photon energy $h\nu$. The band gap energy (E_g) was calculated with the following equation:

$$E_g = \frac{hc}{\lambda_g} \quad (2)$$

where h is Planck's constant, λ_g is the wavelength, and c is the velocity of light. The calculated values of the band gap and direct allowed transition and indirect allowed transition energies for the Ppy thin films irradiated by the oxygen beam and γ rays are shown Table II. The number of carbon hexagon rings in the cluster (N) was calculated with the Robertson relation²³:

TABLE II
Variations in the Band Gap in the Ppy Films

O ⁺⁷ -ion fluence (ions/cm ²)	Band gap (eV)	Conductivity (S/cm)	γ-ray dose (Gy)	Band gap (eV)	Number of carbon atoms per cluster	
					O ⁺⁷ -irradiated	γ-irradiated
Pristine	3.4	40	Pristine	3.4	102	102
3 × 10 ¹⁰	—	—	6.8	3.4	—	102
1 × 10 ¹¹	3.3	52	12	3.4	108	102
3 × 10 ¹¹	3.2	75	30	3.3	115	115
1 × 10 ¹²	3.0	90	67	3.3	131	115

$$E_g(\text{eV}) = 2\beta/\sqrt{N} \quad (3)$$

where 2β is the band structure energy of a pair of adjacent π sites and was taken as about 2.9 eV for a six-numbered carbon ring. From the Robertson's relation, the cluster size was calculated,²⁴ and then, the following relation was used to calculate the number of carbon atoms per cluster:

$$E_g(\text{eV}) = 34.3/\sqrt{N} \quad (4)$$

where N is the number of carbon atoms per cluster in the irradiated polymers. The calculated values of the carbon atoms per cluster in the pristine

and ion-beam-irradiated polymer films are listed in Table II.

SEM

The surface morphological studies of the Ppy films carried out by SEM are presented in Figure 5. A grainlike structure was observed in the unexposed Ppy thin films. The size of the grains depended on the energy loss during interaction. After irradiation with SHI, a microcrystalline structure was seen at a fluence of 3×10^{10} ions/cm². However, a higher fluence of 3×10^{11} and 3×10^{12} ions/cm² exhibited growth of the grainlike structure after irradiation. The grainlike structure growth upon SHI irradiation

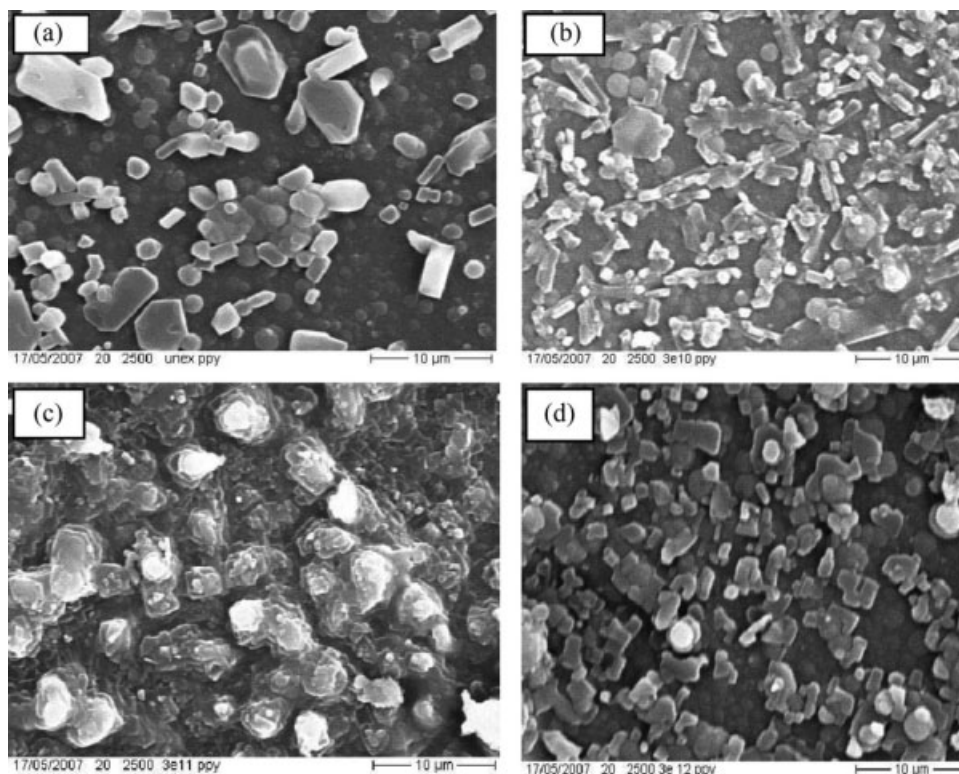


Figure 5 SEM images of Ppy films: (a) pristine film and films irradiated with the O⁺⁷-ion beam at fluences of (b) 3×10^{10} , (c) 3×10^{11} , and (d) 3×10^{12} ions/cm².

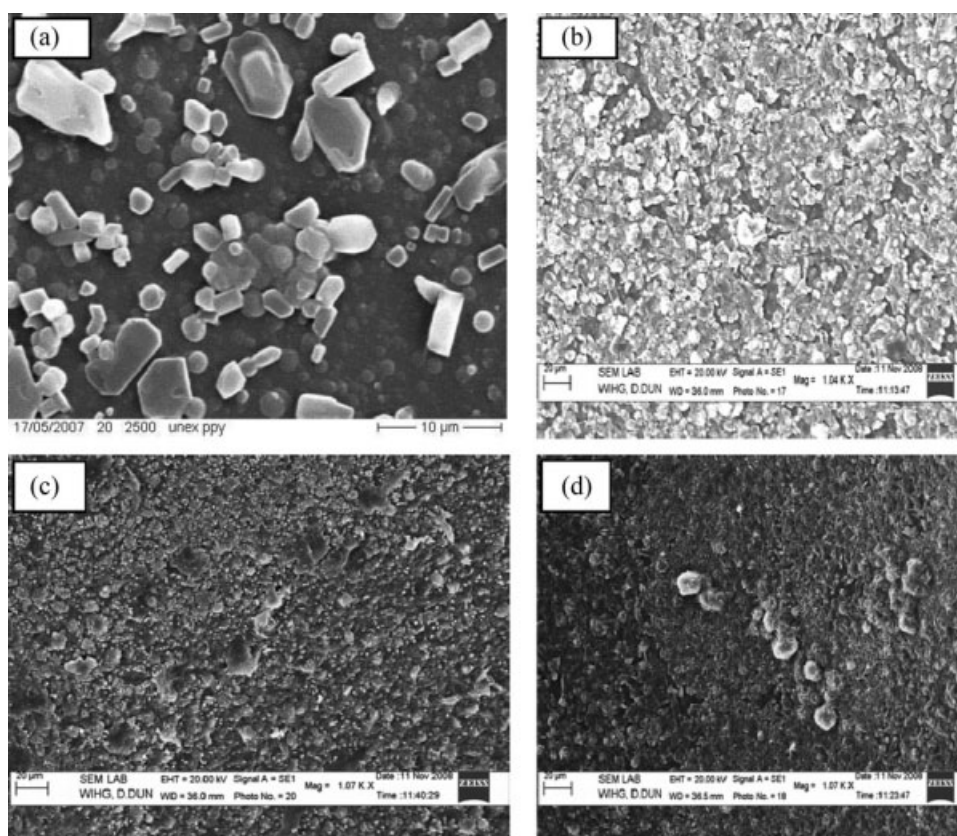


Figure 6 SEM images of the (a) unexposed Ppy films and Ppy films exposed to γ -ray doses of (b) 12, (c) 30, and (d) 67 Gy.

may have been due to huge energy deposition by heavy ions by the process of electronic energy loss. The SEM images (Fig. 6) of the Ppy films showed the microcrystalline structures at a high dose of γ rays.

CONCLUSIONS

The effect of SHIs and γ rays on the structural, optical, and morphological properties of Ppy films were studied in detail. The degree of crystallinity of the polymer films increased with increasing fluence; this may have occurred because of the cross-linking of bonds and the formation of single and multiple helices. The crystallinity of the polymer films was found to improve with increasing ion fluence and γ -ray dose. The intensity of the polaron peak increased with increasing ion fluence. However, the shifting of the peak toward a higher wavelength indicated an increase in the carrier concentration and a reduction in the energy band gap after SHI irradiation. This may have been due to huge amount of electronic energy loss of the heavy ions. No significant change in the band gap was observed after γ -ray irradiation. SEM study showed

the growth of grainlike structures in the Ppy film after irradiation.

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