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## Swift Heavy Copper (50 MeV) Ion Induced Structural Modifications of Polystyrene.

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### ABSTRACT

Polystyrene (PS) films were irradiated with copper (50 MeV) ions, with fluences ranging from  $1 \times 10^{11}$  to  $1 \times 10^{13}$  ions  $\text{cm}^{-2}$  under vacuum at room temperature. Swift heavy ion induced structural modifications were characterized by means of XRD, UV- visible and FTIR techniques. X-ray diffraction study showed that in addition to structural degradation of polymer with the increase of ion fluence there was also an increase of alignment of polymer chains in some of the micro-domains. This behavior was further supported by UV-visible and FTIR results.

**Keywords:** Polystyrene; ion fluence; XRD; UV VIS; FTIR; amorphization and micro-domains.

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## INTRODUCTION

Polymers generally consist of granular structures, which are defined as micro-domains. Micro-domains can be defined as compact zones, of about 5 to 30 nm diameter, of ordered polymeric chains, entrenched in less-dense material with arbitrarily aligned chains. These regions are steadily modified during the swift heavy ion irradiation by formation of radicals, carbon double bonds, de-gassing of unstable components, and cross linking to dense carbon-enriched clusters [1]. Generally, after swift heavy ion irradiation, crystalline phase of many polymers changes to amorphous phase [2-4] but in some exceptional cases, the alignment of polymeric chains after low-fluence ion irradiation has also observed [5].

Hosemann has defined structural behavior of semi-crystalline polymers on the basis of para-crystalline theory [6]. According to this para-crystal theory, the “crystalline” and “amorphous” phases are different components of para-crystals. Different degree of para-crystalline disorder is responsible for different crystallite dimensions. Further, in semi-crystalline polymers, two types of distortions i.e. long and short range order, are present as compared to an ideal, well-ordered crystalline cell [7].

Polystyrene is an organic polymer known for its stability, has found applications as lightweight structural materials in different fields, such in the automotive, aerospace and construction industries. The presence of the phenyl groups/rings prevent the polymer chains from packing into close, crystalline arrangements, hence solid polystyrene is transparent.

In the present investigation, an attempt has been made to investigate the structural modifications in copper (50 MeV) ion induced polystyrene, with emphasis on correlation between the results obtained from the analysis of XRD, UV-visible and FTIR spectra.

## EXPERIMENTAL PROCEDURES

### Materials

PS films of 50  $\mu\text{m}$  thickness were purchased from Good Fellow Ltd. (England) and were used without any modification.

### Irradiation

Readers can find the details of irradiation and irradiation conditions somewhere else (Devgan et. al., 2013). The range of copper (50 MeV) ions in PS was 16.33  $\mu\text{m}$  and their electronic and nuclear energy losses were 529.6 and 1.942 eV/Å, respectively [8].

### Characterization

Three techniques were used to analyze induced effects of swift heavy copper ions in PS. Specific details of techniques has already mentioned in previous paper [2].

## RESULTS AND DISCUSSION

### Structural analysis

Fig. 1 shows the XRD curves of pristine and copper (50 MeV) ion induced polystyrene, at different fluences. It is revealed that in pristine polystyrene, there are two prominent diffraction peaks, at  $2\theta = 9.61^\circ$  (inter-planer spacing  $d_1 \approx 9.20 \text{ \AA}$ ) and at  $18.78^\circ$  ( $d_2 \approx 4.72 \text{ \AA}$ ). The X-ray diffraction patterns and its relevant data in Table 1 indicate that amorphous phase in virgin polystyrene is more as compared to crystalline phase. In addition to this, XRD spectra of irradiated samples reveal some interesting results, which are discussed here.

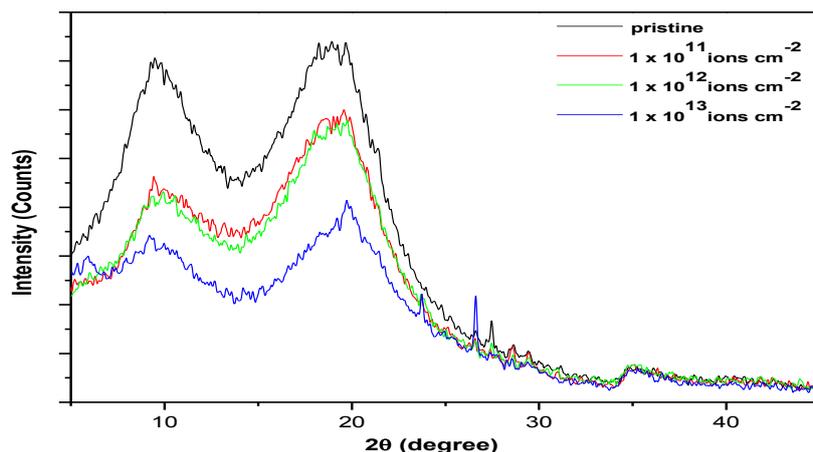


Figure 1: X ray diffraction patterns of copper ion induced polystyrene.

### Discussion on first peak

The intensity of diffraction peaks of polystyrene decreases gradually with the increase of ion fluence. However, the first peak is falling more rapidly as compared to second one. The decrease in intensity of first peak is followed by its broadening, which results in the decrease of average crystallite size,  $L_1$ . The variation of FWHM of first peak ( $\beta_1$ ) with ion fluence is shown in Table 1. The increment of  $\beta_1$  is observed with the increase of ion fluence and hence decrement in the value of  $L_1$ . The decreasing trend of crystallite size,  $L_1$  of the micro-domains related to first peak reveals the increase of amorphization of that particular region. Amorphization is also clearly visible by the rapid fall of intensity of the first peak.

Table 1: Relevant data of XRD spectra (Fig. 1) of pristine and copper (50 MeV) ion induced polystyrene at different ion fluences

Fluence (ions cm <sup>-2</sup> )	First Peak					Second Peak				
	2θ (deg)	β <sub>1</sub> (deg)	L <sub>1</sub> (Å)	d <sub>1</sub> (Å)	I <sub>1</sub>	2θ (deg)	β <sub>2</sub> (deg)	L <sub>2</sub> (Å)	d <sub>2</sub> (Å)	I <sub>2</sub>
0	9.61	5.91	13.50	9.20	803.1	18.78	6.22	12.95	4.72	837.2
1 x 10 <sup>11</sup>	10.01	6.74	11.83	8.83	552.6	19.01	5.91	13.63	4.66	694.6
1 x 10 <sup>12</sup>	9.76	6.78	11.76	9.05	528.4	19.08	5.88	13.70	4.64	674.1
5 x 10 <sup>12</sup>	---	---	---	---	---	---	---	---	---	---
1 x 10 <sup>13</sup>	8.49	8.24	9.67	10.4	437.9	19.68	6.35	12.76	4.51	510.4

Here,  $\beta$  is FWHM,  $L$  is crystallite size,  $d$  is lattice spacing and  $I$  is the intensity of the peak.

It is observed from Table 1 that there is shifting of diffraction peaks. The position of first peak has shifted initially towards higher angle (i.e.  $2\theta = 10.0^\circ$ ) when irradiated with copper (50 MeV) ion at the fluence  $1 \times 10^{11}$  ions cm<sup>-2</sup> and then towards smaller angles with further increase of ion fluence. This is due to the decrease of interplaner spacing,  $d_2$  with increased ion fluence up to certain value where  $d_2$  is minimum, and then the value of  $d_2$  increases with further increment of ion fluence. Minimum value of  $d_2$  is seen for the fluence of  $1 \times 10^{11}$  ions cm<sup>-2</sup>. These results have also been supported in the study of proton irradiated PET fibers [9].

### Discussion on second peak

Some interesting observations can be made from the variation of parameters of the second peak. The intensity of second peak is falling slowly as compared to the intensity of first peak. Here, decrease in intensity

of this peak is followed by its sharpening, except for the samples which are irradiated with highest fluence. The variation of FWHM,  $\beta_2$  of second X-ray diffraction peak with ion fluence is reported in Table 1. The decrement of  $\beta_2$  is observed with the increase of ion fluence and hence increment in the value of  $L_2$ . The increasing trend of crystallite size,  $L_2$  related to second peak may be due to the increase of orderliness/ molecular alignment of polymer chains (which may be to a very small extent) in the micro-domains of that particular region. This regularization could be attributed to chemical modification in some micro-domains assisted by short-range orders. At the fluence of  $1 \times 10^{13}$  ions  $\text{cm}^{-2}$ , there is sudden decrease of crystallite size as shown in table 1, which might be due to overall degradation of the polymer.

It is also obvious from Table 1 that second diffraction peak position shifts towards higher angle with the increase of copper ion fluence, which is due to the decrease of interplaner spacing,  $d_2$  of micro-domains. These results are in contrast with that of [8] wherein the second diffraction peak of proton irradiated polystyrene shifted towards smaller angle at the fluence of  $1 \times 10^{16}$  p/cm<sup>2</sup>.

**UV-visible analysis**

The UV VIS spectra of pristine and irradiated polystyrene are shown in fig. 2. The values of optical band gap and Urbach’s energy have been evaluated [4] and the results are reported in Table 2. The variation of optical band gap with ion fluence is plotted in Fig. 3. There is observed a trend of decreasing energy gap with the increase of ion fluence. The optical energy gap decreases by almost 66.5% in polystyrene at the highest fluence of  $1 \times 10^{13}$  ions  $\text{cm}^{-2}$  on irradiation with <sup>64</sup>Cu ions of 50 MeV.

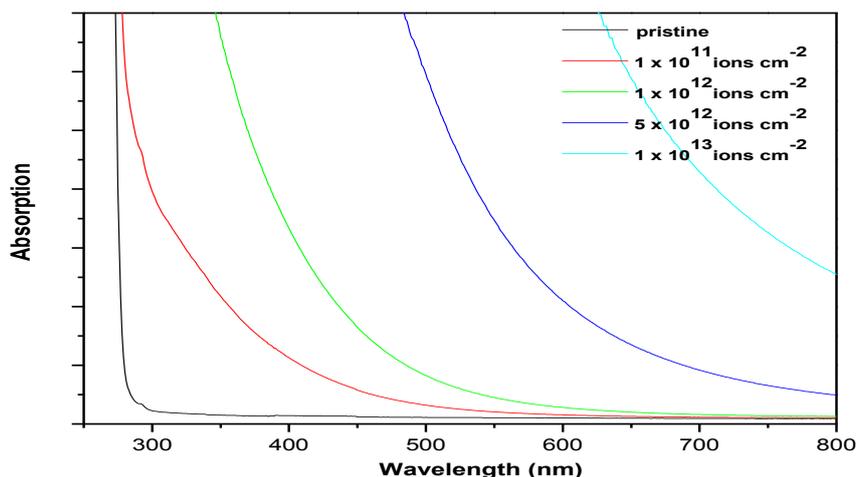


Figure 2: UV-VIS spectra of polystyrene induced with 50 MeV copper ions at different fluences.

**Discussion on optical band gap**

The decrease in optical band gap of polystyrene on copper ion irradiation leads to increase in absorption. The increase in absorption is attributed to the growth of micro-domain boundaries during distortion of polymer on heavy ion irradiation, which results in increase in number of micro-domains. Now if the number of micro-domains are increasing then either the swelling of polymer or decrease in its size will take place. The experimental observation shows no swelling so the later is the only possibility, which ultimately decreases the crystallite size with the increase of ion fluence. These results of UV VIS Spectroscopy are in agreement with the results obtained from our XRD analysis, wherein the FWHM of first peak is increasing and therefore indicating the decrease in crystallite size,  $L_1$  with increase of ion fluence as shown in Fig. 3.

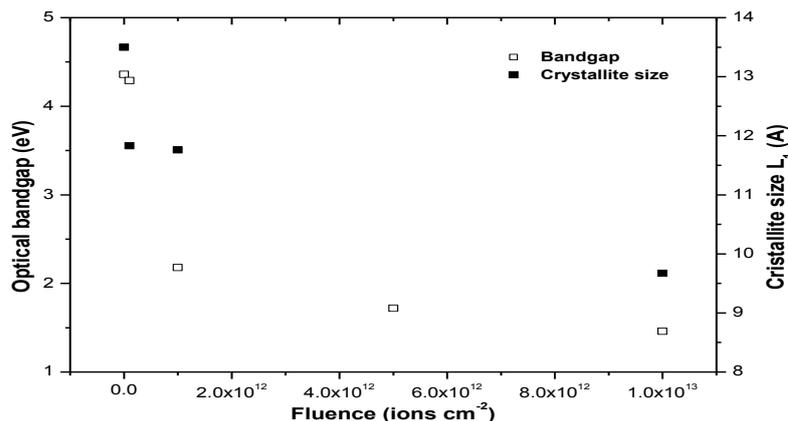


Figure 3: The variation of band gap and crystallite size,  $L_1$  of first X-ray diffraction peak with ion fluence.

### Discussion on Urbach's energy

The irregularities in the band gap level of the polymers are defined in terms of Urbach's energy. The Urbach's tail is generally attributed to the disorder in the material [10]. According to J. Robertson et al. [11] fluctuation of Urbach's energy in amorphous carbon may be because of two types of disorders:

- (i) A structural disorder associated with clusters of the same size but with different amounts of distortion.
- (ii) Topological disorder arising from undistorted clusters but of different sizes.

The variation of Urbach's energy with ion fluence is shown in Fig. 4. The results reveal that in pristine polystyrene, the Urbach's energy has been found to be very small i.e. 0.06 eV. The irregularity in band gap levels of polystyrene suddenly increases to its maximum value (0.67 eV) at the fluence of  $1 \times 10^{11}$  ions  $\text{cm}^{-2}$  (Table. 2), which may be because of increment in domain boundaries. After that it starts decreasing with further increase of ion fluence (i.e. up to  $5 \times 10^{12}$  ions  $\text{cm}^{-2}$ ), which may be attributed to increase of ordering in some micro-domains within this range of ion fluence. At the fluence of  $1 \times 10^{13}$  ions  $\text{cm}^{-2}$ , there is increase of Urbach's energy, which might be due to overall degradation of the polymer. A very good corroboration between Urbach's energy and FWHM,  $\beta_2$  of second X-ray diffraction peak is evident from Fig. 4. It is obvious from Fig. 4 that except for the initial value of  $\beta_2$  and Urbach's energy of pristine polystyrene, rest of the graphs follows almost similar kind of trend with the increase of ion fluence.

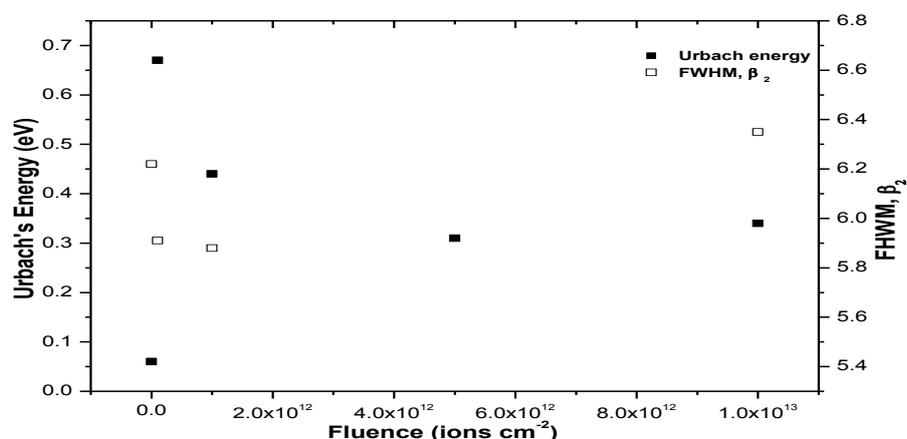


Figure 4: The variation of Urbach's energy and FWHM,  $\beta_2$  of second X-ray diffraction peak with ion fluence.

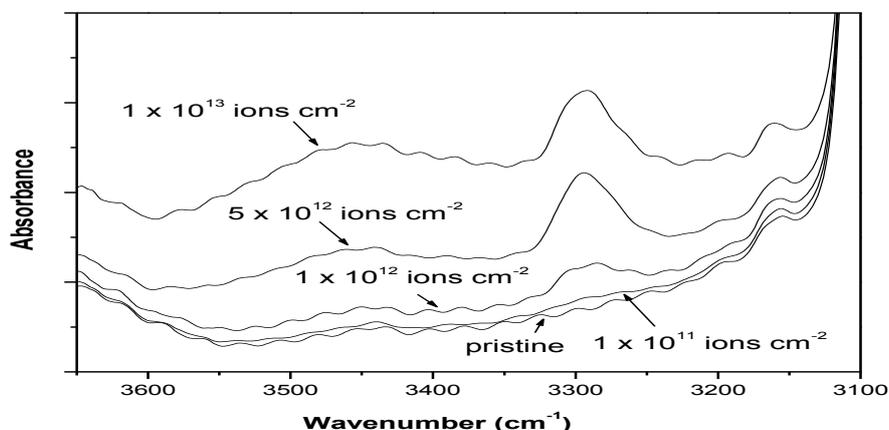
**Table 2: The optical band gap and Urbach's energy of copper (50 MeV) ion induced polystyrene.**

Ions →	Copper ion beam (50MeV)	
Fluence (ion cm <sup>-2</sup> )	Band Gap (eV)	Urbach's Energy (eV)
0	4.36	0.06
1 x 10 <sup>11</sup>	4.29	0.67
5 x 10 <sup>11</sup>	---	---
1 x 10 <sup>12</sup>	2.18	0.44
5 x 10 <sup>12</sup>	1.72	0.31
1 x 10 <sup>13</sup>	1.46	0.34

### FTIR analysis

In order to get more information about the structural modifications of polystyrene we have further analyzed FTIR spectra (Fig. 5) of pristine and copper (50 MeV) ion irradiated polystyrene. Pristine polystyrene has a rich infrared spectrum and in principle, many vibrations could be used to monitor the polymer destruction. We shall restrict ourselves to the alkyne group formation. Specific bands of the trans-configuration of the main chain monitor the amorphization of polymer under ion irradiation. Only the trans-configuration allows dense packing and increases crystalline fraction [12]. A new peak found to appear at 3296 cm<sup>-1</sup> in the FTIR spectra (Fig. 5) of polystyrene after irradiation with copper (50 MeV) ions and it grows with the increase of ion fluence. This new absorption band at 3296 cm<sup>-1</sup> is assigned to R-C≡C-H. The formation of alkyne group is the result of breaking away of phenyl ring at trans-configuration of main chain, as reported earlier [4]. So, alkyne formation in irradiated polystyrene samples more or less is also related to its amorphization. The variation of absorbance at 3296 cm<sup>-1</sup> and FWHM,  $\beta_1$  of first X-ray diffraction peak with ion fluence is shown in Fig. 6. It is observed that alkyne formation and  $\beta_1$  follow almost similar kind of trend with increasing ion fluence. Y. Sun et. al. [13] have also discussed the track radius evolution of amorphization and alkyne formation with ion fluence by means of XRD and FTIR analysis, respectively in PET.

Zigzag planar conformation is the characteristic of syndiotactic polystyrene chains [14]. The absorbance at 1222 cm<sup>-1</sup> has been reported to be related to the zigzag planar sequence and the absorbance at 1183 cm<sup>-1</sup> can be used as an internal reference band. Therefore, the parameter  $R$ , a ratio of the absorbances at 1222 and 1183 cm<sup>-1</sup> can be adopted to follow the growth of conformational order [14]. In Fig. 7, variation of  $R$  and crystallite size,  $L_2$  of second X-ray diffraction peak is plotted as a function of the <sup>64</sup>Cu ion fluence. It can be seen that the structural ordering developed faster at the low ion fluence. This increase of conformational order in our polystyrene samples may be taking place in some micro-domains. It is obvious from Fig. 7 that except for the final value of  $L_2$  (crystallite size of second X-ray diffraction peak) and absorbance ratio,  $R$  of polystyrene, rest of the graphs follows almost similar kind of trend with the increase of ion fluence.


**Figure 5: The evolution of the alkyne (3295 cm<sup>-1</sup>) in FTIR spectra of polystyrene for copper ion irradiation at different fluences.**

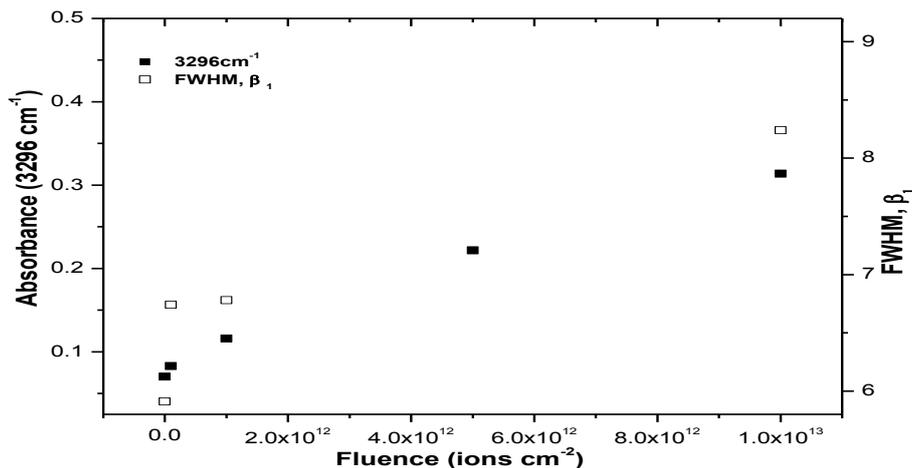


Figure 6: The variation of absorbance band 3296 cm<sup>-1</sup> (alkyne formation) and FWHM, β<sub>1</sub> of first X-ray diffraction peak with ion fluence.

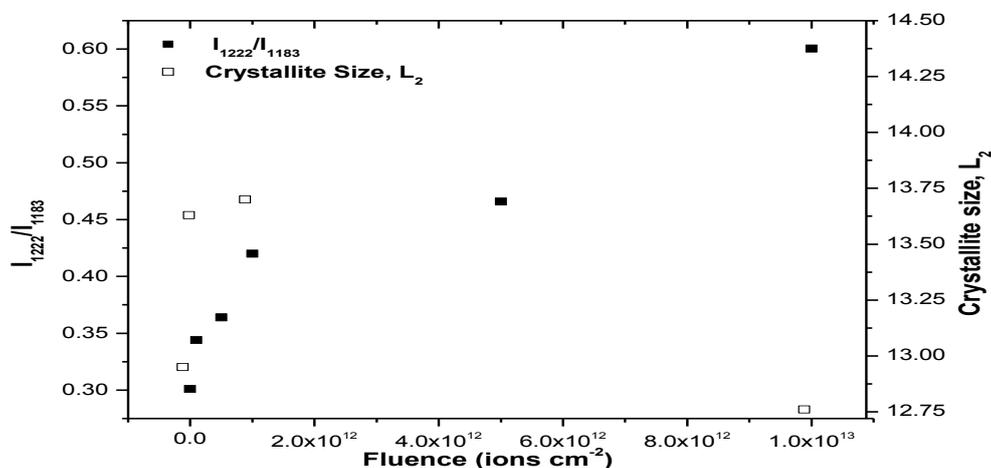


Figure 7: The variation of absorbance ratio I<sub>1222</sub>/I<sub>1183</sub> and crystallite size, L<sub>2</sub> of second X-ray diffraction peak with ion fluence.

### CONCLUSION

XRD, FTIR and UV VIS techniques were applied to investigate the structural modifications of the material. In the present paper it is reasonable to conclude that the increase of amorphization phase in polystyrene is responsible for the increase of FWHM of first X ray diffraction peak, decrease of optical band gap and alkyne formation. Similarly, sharpening of second X ray diffraction peak, decrease of Urbach's energy and increase in the absorbance ratio of I<sub>1222</sub>/I<sub>1183</sub> may be attributed to the increase of ordering (which may to a small extent) in some micro-domains.

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