

Opto-chemical response of CR-39 and polystyrene to swift heavy ion irradiation

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Abstract

The samples of CR-39 and polystyrene (PS) polymers have been irradiated with $^{64}\text{Cu}^{9+}$ (120 MeV) and $^{12}\text{C}^{5+}$ (70 MeV) ion beams having fluence ranging from 1×10^{11} to 1×10^{13} ions/cm². UV spectra of irradiated samples reveal that the optical band gap decreases from 5.50 to 2.75 eV in CR-39 and from 4.36 to 1.73 eV in PS. The correlation between optical band gap and the number of carbon atoms in a cluster with modified Tauc's equation has been discussed in case of CR-39. FTIR spectra reveal that there is the formation of hydroxyl, alkene, alkyne and carboxylic groups in the Cu-ion irradiated PS. In CR-39, changes in the intensity of the bands on irradiation relative to pristine samples without appearance of any new band have been observed and discussed.

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1. Introduction

The importance of polymers has increased very rapidly during the last few decades because of their low cost, easy processability and low weight. The use of ion beams to modify polymer properties, opened a wide area of research and utilization in various fields like industry, agriculture, ecology [1], sensorics [2,3], microelectronics [4] and nanotechnology [5–7]. When a swift heavy ion enters a polymer target, it loses most of its energy in exciting and ionizing the atoms along its trajectory. The high value of energy deposited in a very small cylindrical region around the ion path, called latent track, leads to dramatic modifications in the target material [8–10]. The chemical changes caused by ionizing radiations involve the main-chain scission, cross-linking, creation of free radicals and formation of saturated and unsaturated groups with stimulated evolution of gasses [11].

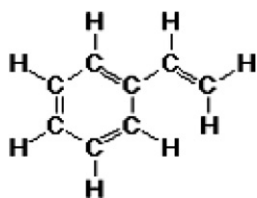
The formation of carbonaceous clusters in polymer films with ion irradiation has been investigated extensively [12–14]. The optical studies of the so called blackening of polymer films can be correlated with the release of carbon atom from the polymer chain during irradiation consequently forming graphite like precipitation or clusters [13]. The previous studies [15] reveal that in the case of high-energy heavy ion impact, the cluster formation sets in at minimum transferred electronic energy density of around 10^{-3} eV/Å³. However, the threshold energy density for low energy heavy ion impact is 10^{-1} eV/Å³. Zeigler et al. [16] suggested highly energetic heavy ions form small clusters along single ion tracks. The cluster size does not exceed the track diameter (10 nm). However, in the case of overlapping of light low energy particles, the cluster size is not limited by the track diameter and giant clusters are formed, exceeding 100 nm in size. For example, in the case of PMMA irradiated with 35 MeV Li with a fluence of 1×10^{12} ions cm⁻², large fractional structures are produced, whereas 2 GeV of Au with a fluence of 5×10^{10} ions cm⁻² in PMMA produces small clusters 5–6 nm in size [16].

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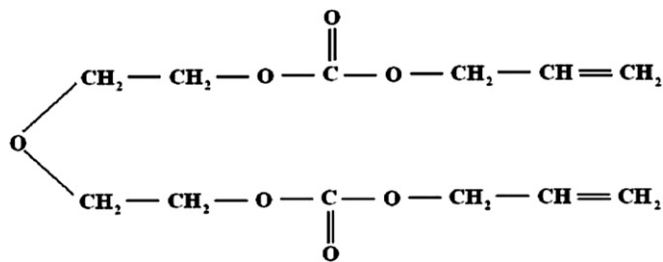
Amorphous carbon or graphite is known to consist of compact clusters of fused sixfold rings (M). The number of such rings in a cluster may be obtained from the optical band gap, E_g , with Robertson's relation [17].

In the present work, polystyrene and CR-39 polymer samples were irradiated with $^{64}\text{Cu}^{9+}$ (120 MeV) and $^{12}\text{C}^{5+}$ (70 MeV) ion beams to investigate their response towards swift heavy ion irradiation with respect to optical and chemical properties. In order to obtain the information about the number of rings (M) in a cluster in PS and the number of carbon atoms per conjugation length (N) in CR-39, UV–Vis spectroscopic technique has been used.

PS is one of the most stable polymers with respect to radiation and very large doses are required to produce any noticeable change [18]. The chemical structure of monomer of polystyrene is given below.



PS contains a large number of benzene rings, which are known to have “protective” action in many radiation-chemical processes. However, heavy ion irradiation of such polymers induces drastic changes in their original structure [19,20]. The monomer of CR-39 is represented as follows:



In polymer form, there exists a three-dimensional network of polyallyl chains cross-linked by diethylene glycol dicarbonate linkages. The branching point in this net is the tertiary carbon in the polyallyl chain [21].

2. Experimental procedures

The specimens of polystyrene (125 μm) and CR-39 (250 μm) in the form of flat polished thin films were obtained from Goodfellow Ltd. (England) and Pershore Moulding Ltd. (England) respectively. These were used as-received form without any further treatment in the size of 1 cm \times 1 cm. The samples were mounted on the sliding ladder and irradiated with $^{64}\text{Cu}^{9+}$ (120 MeV) and $^{12}\text{C}^{5+}$ (70 MeV) ion beams using 15UD pelletron facility in the general purpose scattering chamber (GPSC) under high vacuum of 10^{-6} Torr at Inter-University Accelerator Centre, New Delhi. The electronic stopping power of $^{64}\text{Cu}^{9+}$ (120 MeV) ion in PS and CR-39 is 530.4 and 637.3 eV/ \AA respectively, while for $^{12}\text{C}^{5+}$ (70 MeV) ion in the same targets is 26.9 and 33.4 eV/ \AA respectively [22]. The ion beam fluence was varied from 1×10^{11} to 1×10^{13} ions cm^{-2} . Corresponding to the fluences used, the transferred energy densities, obtained from the dose-power relation, ranged from 10^{-4} to 10^{-1} eV/ \AA^3 . In order to expose the whole target area, the beam was scanned in the x – y plane. The beam current was kept low to suppress thermal decomposition and was monitored intermittently with a Faraday cup. Other implant conditions are summarized in Table 1. The samples were analyzed with UV–Vis spectroscopy using Hitachi Modal U-3000 spectrophotometer in the range 200–800 nm to observe the variation in optical band gap and Urbach's energy. The chemical-changes were studied using Nexus 870 FTIR Spectrometer in the range 4000–500 cm^{-1} .

Table 1
Irradiation conditions for polystyrene and CR-39

Sr. No.	Sample	Ion, energy and charge state	Fluence (ions cm^{-2})	Current (pA)	Comment
1	PS-0	Cu, 120 MeV, +9	0	0	Transparent
2	PS-1	Cu, 120 MeV, +9	1×10^{11}	$1 \pm .08$	Pale yellow
3	PS-2	Cu, 120 MeV, +9	5×10^{11}	$1 \pm .08$	Yellow
4	PS-3	Cu, 120 MeV, +9	1×10^{12}	$1 \pm .08$	Brown
5	PS-4	Cu, 120 MeV, +9	5×10^{12}	$1 \pm .08$	Dark brown
6	PS-5	Cu, 120 MeV, +9	1×10^{13}	$1 \pm .08$	Black & brittle
7	PS-6	C, 70 MeV, +5	1×10^{11}	$2 \pm .04$	Transparent
8	PS-7	C, 70 MeV, +5	5×10^{11}	$2 \pm .04$	Translucent
9	PS-8	C, 70 MeV, +5	1×10^{12}	$2 \pm .04$	Pale yellow
10	PS-9	C, 70 MeV, +5	5×10^{12}	$2 \pm .04$	Yellow
11	PS-10	C, 70 MeV, +5	1×10^{13}	$2 \pm .04$	Light brown
12	CR-0	Cu, 120 MeV, +9	0	0	Transparent
13	CR-1	Cu, 120 MeV, +9	5×10^{11}	$1 \pm .08$	Pale yellow
14	CR-2	Cu, 120 MeV, +9	5×10^{12}	$1 \pm .08$	Yellow
15	CR-3	C, 70 MeV, +5	1×10^{11}	$4 \pm .02$	Translucent
16	CR-4	C, 70 MeV, +5	5×10^{11}	$4 \pm .02$	Pale yellow
17	CR-5	C, 70 MeV, +5	1×10^{12}	$4 \pm .02$	Yellow
18	CR-6	C, 70 MeV, +5	5×10^{12}	$4 \pm .02$	Light brown
19	CR-7	C, 70 MeV, +5	1×10^{13}	$4 \pm .02$	Brown

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