

$^{12}\text{C}^{5+}$ radiation effects in SR-86 track recording polymer

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Abstract. The samples of SR-86 polymer were irradiated with $^{12}\text{C}^{5+}$ ions of energy 5.0 MeV/u using fluences of 10^{11} – 10^{14} ions/cm² at NSC Pelletron in a high vacuum scattering chamber. The optical studies show an increase in absorption of UV or IR in the shorter wavelength region (250–500 nm). The study also reveals that the increase in radiation dose extends the optical absorption region to longer wavelengths. It is observed that the bulk etch rate of this polymer is enhanced after heavy ion irradiation.

Keywords. SR-86 polymer; IR spectra; UV spectra; optical absorption; bulk etch rate; AFM.

1. Introduction

The importance of polymers has increased very rapidly during the last few decades because of their low cost, easy processability, low weight, high quality surfaces and easy fabrication of thick and thin samples, etc. Once the most valued property of polymers was their capacity to inhibit electrical conduction as insulators, now they are attracting considerable attention as conducting polymers (Itoh *et al* 1973). Due to their ease of handling, they can be easily used as thin films to guide optical waves or as thick films in holographic recording media (Manivannan and Lessard 1994).

Heavy ion irradiation of polymers resulted in many physical and chemical changes, e.g. density (Calcagno and Foti 1987), conductivity (Davenas *et al* 1990), optical absorption (Mazzoldi and Arnold 1987), molecular weight distribution and solubility (Licciardello and Puglisi 1994), etc which cannot be achieved by the routinely synthetic way. These changes depend on target parameters (composition, molecular weight, temperature, etc) and on ion beam parameters (energy, mass and fluence). The primary phenomena associated with ion–polymer interaction are cross-linking, chain scission and emission of atoms, molecules and molecular fragments (Chapiro 1988). These modifications have imparted many technological implications in microlithography, microelectronics, optoelectronics, communication devices, etc (Spohr 1990; Franke 1992). The various scientific and technological applications of polymers are due to their structural, mechanical and thermal stability.

Optical properties of polymers have been characterized by various workers (Elman *et al* 1985; Fink *et al* 1988) by correlating the change in optical properties with the mode of energy deposition. Marletta *et al* (1989) have found a correlation between chemical structure modifications and change in electrical properties by some polymers. Improvements in surface smoothness, hardness and wear resistance of polymers by multiple ion irradiation has been studied by Lee *et al* (1991). The aim of the present investigations is to study the change in chemical behaviour, nature of radiation damage, change in optical properties and morphology of radiation damaged surface of SR-86 polymer commonly used as a nuclear track recorder.

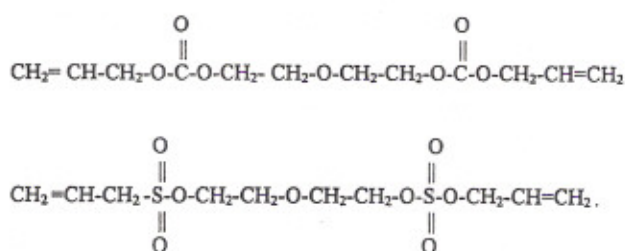
Heavy ion irradiations of insulators lead to damaged zones, created along the path of the fast heavy ion, are called latent tracks. The size, shape and internal structure of these tracks resulted from many primary processes which are not directly observable. In the recent past, various techniques have been used for the investigations of morphology, surface and structure of latent tracks in solids such as neutron and X-ray scattering (Albrecht *et al* 1985), transmission electron microscopy (Scholz *et al* 1993) and scanning tunneling microscopy (Coratger *et al* 1990). In the past few years, several scanning probe microscopes (SPM) have been developed such as photon scanning tunneling microscope (Ferrell *et al* 1991), scanning ion microscope (Hausma *et al* 1989), magnetic force microscope (Martin and Wickermasinghe 1987) and atomic force microscope (AFM) (Binnig *et al* 1986). Atomic force microscope has an important advantage over other microscopes that images can be obtained for conducting as well as insulating surfaces on a nanometer scale. A sharp tip attached to a flexible microlever

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interacts with the surface underlying via contact forces. In the so called topographical mode, the AFM is sensible to the forces causing cantilever move up and downward while the tip follows the surface corrugation. In addition, lateral forces caused by friction result in a torsion of the lever around its long axis.

2. Experimental

Polymer SR-86 (Fukuvi Co. Ltd., Japan), is of common use as a heavy ion track recorder due to its high charge resolution and sensitivity (Fujii *et al* 1991). It is a copolymer of diethylene glycol bis of allyl sulphonate (DEAS) and CR-39 in the ratio 20 : 80, respectively. Monomer of CR-39 and DEAS are respectively, given by



DEAS monomer was synthesized by condensation of diethylene glycol and allyl sulphonyl chloride in the presence of pyridine.

Heavy ion irradiation was carried out at Nuclear Science Centre (NSC), New Delhi, using a 60 MeV $^{12}\text{C}^{5+}$ ion beam available from 15 UD Pelletron accelerator. Samples of polymer films (2 cm^2) were prepared as targets and mounted on a target ladder before irradiation. Six targets were irradiated in a single mount in a general purpose scattering chamber (GPSC) evacuated to 10^{-6} mbar. The ion beam fluence was varied from 10^{11} to 10^{14} ions/ cm^2 (with a beam area of $1.6 \times 1.2\text{ cm}^2$) during irradiation in different runs by changing the targets for each run. All targets were exposed at room temperature using normal incidence in GPSC.

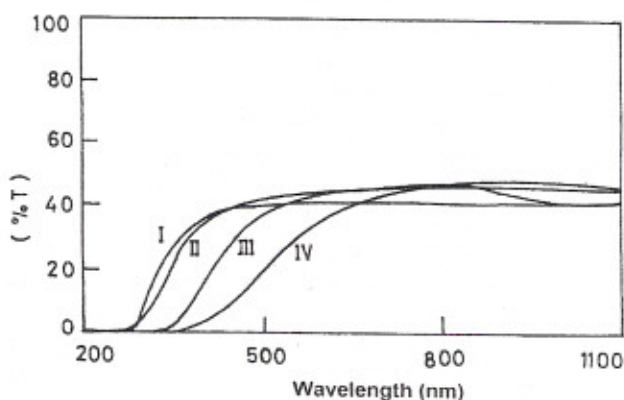


Figure 1. UV visible spectra of SR-86 sample irradiated with $^{12}\text{C}^{5+}$ at different doses (I – virgin, II – 10^{11} , III – 10^{12} and IV – 10^{13} ions/ cm^2).

The nature and extent of radiation damage, or in other words, structural modifications in polymers can be characterized by different techniques such as UV visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, ultraviolet photoemission spectroscopy (UPS), electron energy loss spectroscopy (EELS), Rutherford backscattering (RBS) and solubility measurements. We have used the first two techniques for our characterization and the spectrophotometers employed are UV visible-166 and FTIR-8101M (Shimadzu, Japan).

3. Results and discussion

Heavy ion-polymer interaction is a complex process where a lot of primary and secondary effects are involved. In a short time (10^{-15} s), the ion energy is transferred to the electrons in the polymer chain within a small volume surrounding the ion track. Due to a large amount of energy transfer to the electronic-molecular environment

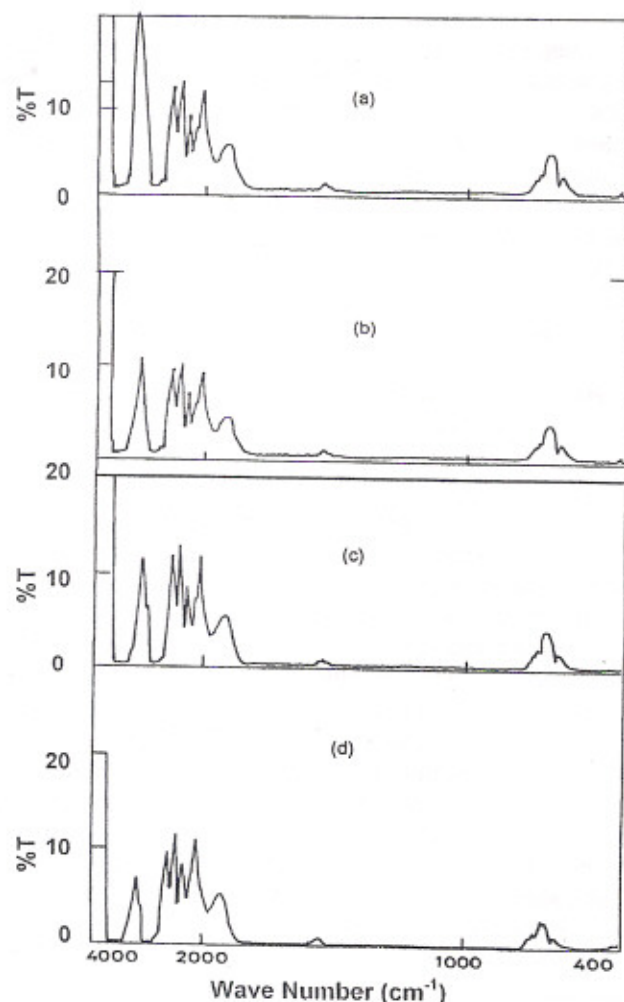


Figure 2. IR spectra of SR-86 irradiated with $^{12}\text{C}^{5+}$ at different doses (a) virgin, (b) 10^{11} , (c) 10^{12} and (d) 10^{13} ions/ cm^2 .

in polymers, the energy spike induces breaking of original bonds, production of excited and ionized species of radicals and bonds rearrangement which are responsible for most of the observed chemical modifications.

Figure 1 shows the UV visible spectra of SR-86 for three different irradiation doses in comparison to an unexposed sample. It is observed that there is an increase in optical absorption in the short wavelength range (250–500 nm) after heavy ion irradiation. The region of optical absorption extends to higher wavelengths for higher irradiation doses. The reversal effect also disappears at a fluence of 10^{13} ions/cm² (Calcagno *et al* 1992). It proves that radiation damage effects are complex and non-linear in this most sensitive nuclear track recording polymer.

To further investigate the nature and extent of radiation damage in SR-86, recourse is taken to FTIR spectroscopy. The optical absorption results of IR spectra of SR-86 are

shown in figure 2. The comparison of IR spectra of unirradiated and irradiated samples indicates that the infrared absorption increases around 3600 cm^{-1} . This absorption can be assigned to the terminal O–H end groups which may have formed due to cross linkings. This may be due to evolution of CO_2 and SO_2 during the irradiation process. If CO_2 is evolved on irradiation the possible structure after irradiation may be represented as

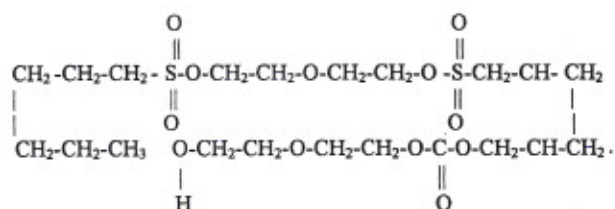


Table 1. Bulk etch rates of polymers (CR-39, SR-86 and Makrofol-KG), measured by thickness measurement method ($V_b = \Delta x/2 t$).

Samples	Etchant conc.	Etching time	Etchant temperature	Bulk etch rate ($\mu\text{m/h}$)	
				Unirradiated	Irradiated
CR-39	6.25 N NaOH	2 h	60°C	1.25	1.75
SR-86	6.25 N NaOH	2 h	60°C	2.00	3.50
Makrofol-KG	6.25 N NaOH	2 h	60°C	0.75	1.00

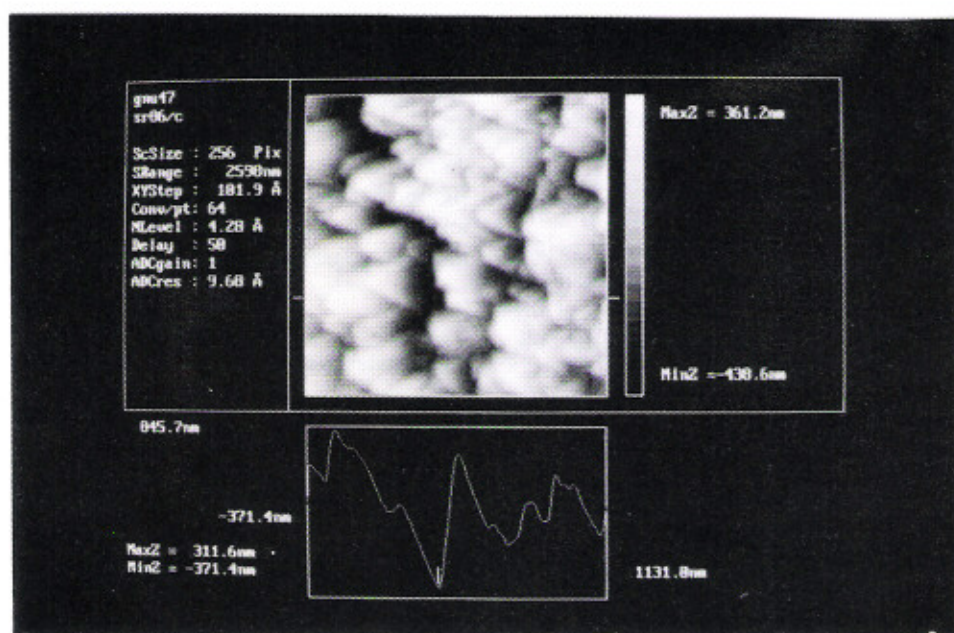


Figure 3. AFM scanned surface morphology of SR-86 track recording polymer irradiated by ^{12}C (5.0 MeV/u).

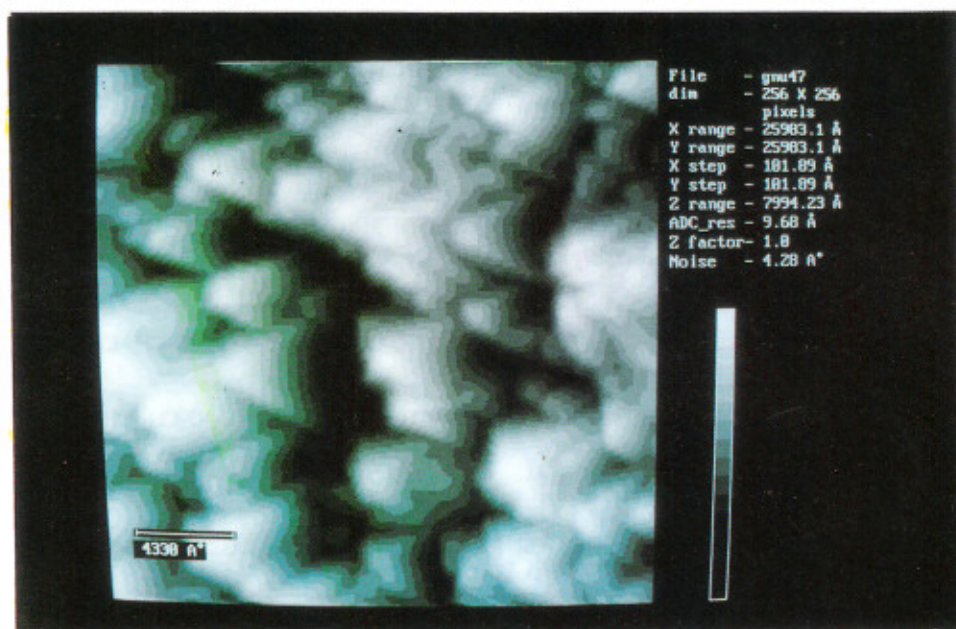
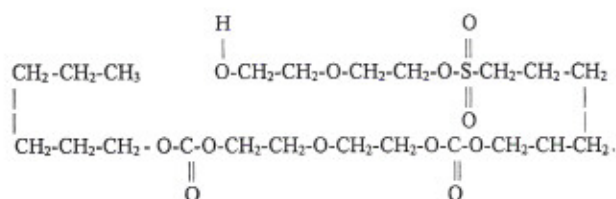


Figure 4. An enlarged view of the radiation damaged surface of SR-86 scanned under AFM.

If SO_2 is evolved on irradiation, the possible structure after irradiation is



Both irradiated and unirradiated polymer samples (SR-86, Makrofol-KG and CR-39) were etched in the laboratory under identical conditions using 6.25 N NaOH solution at 60°C for 2 h in a constant temperature bath. The bulk etch rates were measured (Durrani and Bull 1987) by 'thickness measurement method'. In this technique, the thickness of the sample is measured before and after etching for a certain period of time using a sensitive micrometer. If y and y' be the thickness of the sample before and after etching for a time, t , then the bulk etch rate, V_b is given by

$$V_b = (y - y') / 2t.$$

The bulk etch rates of CR-39, SR-86 and Makrofol-KG polycarbonate are summarized in table 1. It is observed that bulk etch rates of all polymers are enhanced after irradiation and the maximum effect is noticed in SR-86. The dissolution rate of bulk material is affected by the available free energy associated with the creation of damage zones around the ion path. A similar observation was made by Bhatia *et al* (1990) on CR-39.

The direct image of the surface morphology of the latent tracks made by AFM gives new information on track formation and its structure and size. With this technique it is possible to reach up to atomic resolution and to produce 3-D images of heavy ion impacts on the surface of material. The surface of the irradiated and very slightly etched samples of SR-86 have been investigated under atomic force microscope at the Central Scientific Instruments Organization (CSIO) at Chandigarh. Figure 3 shows the surface morphology of SR-86 polymer irradiated by ^{12}C (5.0 MeV/u) heavy ions with fluence of 10^{14} ions/cm² and etched in 6.0 N NaOH solution for 8 min at room temperature. Due to a high fluence of carbon beam no single ion impact is observable in this figure. Figure 4 shows an enlarged view of the same microphotograph. A large damage zone is visible in this microphotograph.

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