

Modification of Polyethersulphone Induced by High Energy Proton, C⁺, and Ne⁶⁺ Ions: A Spectroscopic Study

S. Vinodh Kumar, B. Ghadei, P. K. Jal, K. Dey, J. B. M. Krishna, A. Saha

UGC-DAE Consortium for Scientific Research, Kolkata Centre, III/LB-8 Bidhannagar, Kolkata 700098, India

Received 23 February 2005; accepted 18 October 2005

DOI 10.1002/app.23552

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyethersulphone (PES) was irradiated with 4 MeV proton, 3.6 MeV C⁺, and 145 MeV Ne⁶⁺ ions at different ion fluences. The linear energy transfer dependence on ion-induced spectral changes was analyzed by ultraviolet–visible, Fourier transform infrared spectroscopy and fluorescence spectroscopy. The gradual red shift with the increase in optical absorption was observed in the region of 350–500 nm for proton and 400–800 nm for C⁺ and Ne⁶⁺ ions irradiated PES. The gradual shift in absorption may be attributed to the formation of carbonaceous clusters. The gradual decrease in optical band gap indicates increase in

cluster sizes. When PES was irradiated with protons, loss in fluorescence emission intensity at 440 nm was observed, although there was no change in spectral shape. In contrast, C⁺ and Ne⁶⁺ ion irradiated PES showed blue shift with concomitant loss in intensity and the formation of new peak at 575 nm. In fact, heavier ions are found to be more effective in inducing physicochemical modifications in PES. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1591–1597, 2006

Key words: polyethersulphone; heavy ions; irradiation; high LET; luminescence

INTRODUCTION

The modification of polymeric materials using ion beam explores the usage of polymers in various fields like hard radiation encountered in nuclear power plants, spacecrafts, sterilization irradiators, high energy particle accelerator, etc.¹ Microdevice production (lithography) is another exciting application of polymer radiation processing that is now emerging in production of microelectronic circuits and ultrasmall circuits.²

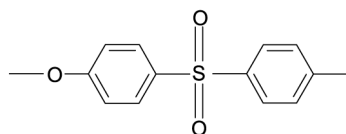
Ion beam irradiation has been found to be widely applicable in modifying the structure and properties of polymers and it is possible to control the ion-induced modification of properties of the polymers using the parameters like the ion fluence, flux, dose rate, etc. Particularly, some unique modifications like the creation of different unsaturated products ranging from isolated alkenes and alkynes to big molecules such as fullerenes (clusters) are possible under high energy heavy ion [high linear energy transfer (LET)] bombardment in polymer structure, which are never observed when using electrons or gamma rays (low LET).³ Carbonaceous clusters that are supposed to be carriers in electrical conductivity are formed along latent tracks of energetic ions in polymers. Several extensive studies had been done in the formation of

carbonaceous clusters with ion irradiation.^{4,5} Ultraviolet–visible (UV–vis) spectrometry is a sensitive tool to investigate the optically absorbing clusters. These peculiarities of the interactions between heavy ions and high molecular weight substances have attracted considerable attention in recent years.^{6–9}

When an energetic ion traverses a polymer medium, it loses energy by two main processes, namely, electronic and nuclear stopping. The electronic stopping is largely responsible for crosslinking and nuclear stopping for scission, although both processes can cause crosslinking as well as scission. The most important parameter for crosslinking is found to be LET.¹⁰ It is important to know the LET effects of materials to be used in space technology to examine their durability when exposed to different types of radiation.¹¹

The major chemical changes in polymers when subjected to ionizing radiations are gas evolution (H₂ etc), creation of new double bonds (formation of unsaturation), main chain scission (C[single bond]C bond scission), and radical–radical combination (crosslinking).¹² The main chain scission, side chain cleavage, and the formation of three-dimensional network like structure had been found in our previous studies on polypropylene with ionizing radiation.^{13,14} To extend our previous studies, we have chosen polyethersulphone (PES) for our present study because of its wide range of applications. PES is engineering thermoplastic with excellent high temperature properties. The radiation-induced chemical modification of polysulphones is an outstanding topic, owing to the many different applications of these polymer materials in

Correspondence to: Dr. A. Saha (abhijit@alpha.iuc.res.in).



Scheme 1

various fields involving the interaction with energetic particles. Thus, for instance, aliphatic poly(olefin sulfone)s are important for their growing applications because of the unusually high lithographic sensitivity to ionizing radiations, while aromatic polysulphones have wide applications in the aerospace industry as thermo- and radiation-resistant materials.^{15,16}

The study of the evolution of photoemission and the radiation damage under ion irradiation is a primary topic in the development of radiation hard polymer based scintillators.¹⁷ Until now, the optical properties of irradiated polymers have been mainly studied by optical absorption. The luminescence property under irradiation has been studied only in few cases.^{18,19} This has prompted us to investigate the changes in luminescence vis-à-vis absorption profile of PES because of ion beam irradiation.

MATERIALS AND METHODS

Materials

PES of 1.5 mm thickness and high-grade quality sheet was purchased from Good fellow Metals Limited (UK). The density of the sample was 1.37 g/cm³. The monomeric unit of PES has the following structure (Scheme 1).

Ion beam irradiation

The polymer samples were cut into 2 × 2 cm² small pieces for irradiation. The proton and C⁺ ion irradiation was carried out by using the irradiation facility with 3 MV tandem Pelletron at the Institute of Physics, Bhubaneswar, India, the beam energy being used 4 MeV and 3.6 MeV, respectively. The Ne⁶⁺ ion irradiation was done by using the irradiation facility with Cyclotron accelerator at VECC, Kolkata, India, and the beam energy was 145 MeV. The used range of ion fluences were in the order of 10¹² to 10¹⁴ ions/cm². The ion current was measured during irradiation of insulating samples using a faraday cup or current integrator connected to the sample holder. The current was kept around 5 nA to avoid the heating of the sample. The ion beam was scanned or diffused across an area of 1 × 1 cm² to have a homogenous irradiation.

Determination of stopping power and penetration range

The maximum penetration of three different ions used into PES was determined using the transport of ions in matter code. Simulation by SRIM 2003 showed that the maximum penetration ranges of the three different ions on PES were 215.11 μm, 5.29 μm, and 152.11 μm for protons, carbon, and neon ions, respectively. The electronic stopping powers (dE/dX)_{elec} of the different beams in PES were also deduced, which were 0.11 × 10², 9.91 × 10², and 6.46 × 10² KeV/μm, respectively.

Spectroscopic measurements

The UV-vis spectral measurements of the pristine and irradiated polymer samples were carried out with spectrophotometer (Schimadzu UV-1601 PC). The fluorescence emission of pristine and irradiated samples was monitored with Luminescence spectrometer (Perkin-Elmer LS-55), with both excitation and emission bandpass of 5 nm. The Fourier transform infrared (FTIR) spectral measurements of the polymer samples were carried out using Perkin-Elmer FTIR system (Spectrum GX) in 20 scans with the data interval 0.5 nm, and the resolution was 2 cm⁻¹.

RESULTS AND DISCUSSION

UV-vis absorption spectroscopy

The optical absorption spectra of proton irradiated PES (Fig. 1) show the gradual increase in the optical absorption and the shift from the near UV to the Visible region with increase in ion fluence. From the

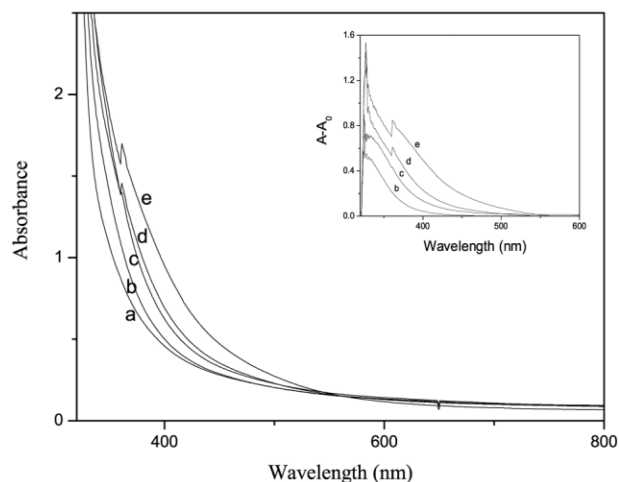


Figure 1 Absorption spectra and difference absorption spectra (inset) of polyethersulphone unirradiated and irradiated with 4 MeV H⁺ ions at different fluences; (a) Pristine; (b) 2 × 10¹³ ion/cm²; (c) 5 × 10¹³ ion/cm²; (d) 1 × 10¹⁴ ion/cm²; (e) 2 × 10¹⁴ ion/cm².

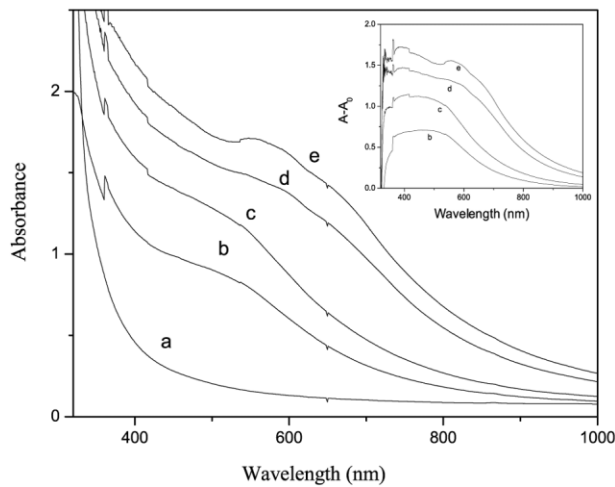


Figure 2 Absorption spectra and difference absorption spectra (inset) of polyethersulphone unirradiated and irradiated with 3.6 MeV C^+ ions at different fluences; (a) Pristine; (b) 5×10^{13} ion/cm 2 ; (c) 7.5×10^{13} ion/cm 2 ; (d) 1×10^{14} ion/cm 2 ; (e) 1.5×10^{14} ion/cm 2 .

difference absorption spectra (Fig. 1, Inset), the growth of absorption due to proton irradiation was found in the region of 350–500 nm. The irradiated polymer surfaces show the visible color change from amber to yellowish. But in case of C and Ne ion irradiated PES, although increase in absorption was observed, peaks are more red shifted (Figs. 2 and 3) and growth in absorption was in the region of 400–800 nm (Insets of Figs. 2 and 3). The visible color was also found to change from amber to yellowish and then brownish with increase in ion fluence. The increase in absorption due to irradiation with high energy ions was reported in some polymeric systems.^{20–22} The observed results indicate the formation of new chromophoric groups having maximum absorption near visible regions.

The significant shift in the optical absorption from the near UV to the Visible region can result in change in optical band gap E_g .²³ Band gap energy can be derived by the following Tauc's expression [eq. (1)]:²⁴

$$\omega^2 A = (\hbar \omega - E_g)^2 \quad (1)$$

where A is optical absorbance and ω is the angular frequency, which equals to $2\pi c/\lambda$ (c = speed of light, λ = wavelength). The E_g values can be obtained by plotting $A^{1/2}/\lambda$ versus $1/\lambda$. The intersection of the extrapolated curve with the abscissa gives the band gap wavelength λ_g and from the data the optical absorption band gap energy can be calculated by using the following expression [eq. (2)]:

$$E_g = hc/\lambda_g \quad (2)$$

Using Tauc's plot, optical band gap has been determined for pristine PES and samples irradiated with different ions at varied ion fluences. The results are shown in Table I. The optical band gap energy value shows a gradual decrease with the increase in ion fluence for three different ions. However, from Table I, it is apparent that high LET radiations, namely, C^+ and Ne^{6+} ion beam, have more effect on optical bandgap compared with that caused by low LET proton. This supports the previous reported changes in other systems, e.g., polymethylmethacrylate and polyethyleneterephthalate.^{25,26}

Robertson and coworkers correlated the value of optical band gap energy with the number, type, and structural arrangements of the carbon bonds per molecule or per compact cluster.²⁷ Accordingly, in case of polymers with linear chain structure (e.g., polyethylene or polypropylene), the shift in optical absorption from near UV to the Visible region could be attributed to an increase of the conjugation length, whereas for polymers containing aromatic rings (e.g., polyimide or polyethyleneterephthalate), condensation into compact clusters might be the more probable explanation. The number of carbon hexagon rings in the cluster, M , can be derived from the Robertson's correlation between E_g and M [eq. (3)].

$$E_g = 2|\beta|M^{-0.5} \quad (3)$$

where 2β is the band structure energy of a pair of adjacent π sites and β is -2.9 eV for a six-member carbon ring. Fink et al.⁴ showed that the Robertson formula underestimates the cluster size in irradiated polymers. Therefore, they evaluated a new relation

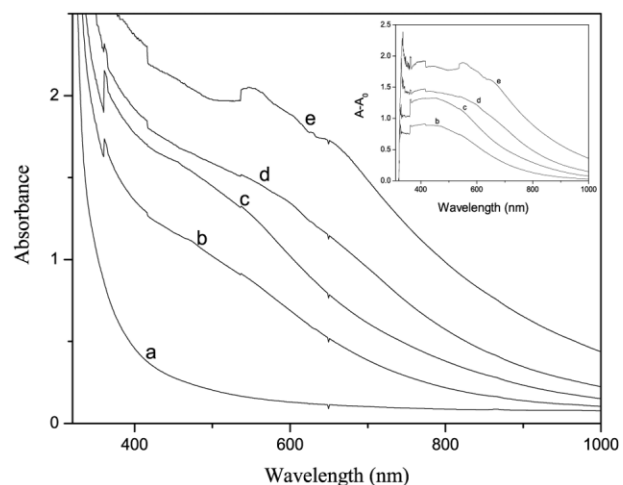


Figure 3 Absorption spectra of and difference absorption spectra (inset) of polyethersulphone unirradiated and irradiated with 145 MeV Ne^{6+} ions at different fluences; (a) Pristine; (b) 4.22×10^{12} ion/cm 2 ; (c) 8.33×10^{12} ion/cm 2 ; (d) 1.66×10^{13} ion/cm 2 ; (e) 3.33×10^{13} ion/cm 2 .

TABLE I
Optical Band Gap Energies and Cluster Sizes of Polyethersulphone Irradiated With 4 MeV H⁺, 3.6 MeV C⁺, and 145 MeV Ne⁶⁺

Energy, projectile	Ion fluence (ions/cm ²)	E_g [eV]	Cluster size	Mean electronic energy density [eV/Å ³]
Pristine	0	3.46	98	0
4 MeV H ⁺	2×10^{13}	3.19	116	0.22×10^{-2}
	5×10^{13}	2.99	132	0.55×10^{-2}
	1×10^{14}	2.94	136	0.11×10^{-1}
3.6MeV C ⁺	2×10^{14}	2.72	159	0.22×10^{-1}
	5×10^{13}	2.58	177	4.96×10^{-1}
	7.5×10^{13}	2.50	188	7.43×10^{-1}
	1×10^{14}	2.39	206	9.91×10^{-1}
	1.5×10^{14}	2.29	224	1.49×10^0
145MeV Ne ⁶⁺	4.22×10^{12}	3.32	107	2.73×10^{-2}
	8.33×10^{12}	3.08	124	5.38×10^{-2}
	1.66×10^{13}	2.87	143	1.07×10^{-1}
	3.33×10^{13}	2.57	178	2.15×10^{-1}

using the clusters of naturally existing carbon clusters with a well-defined and known number of carbon atoms per cluster, such as buckminsterfullerenes, C₆₀ with $N = 60$ [eq. (4)].

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

where N is the number of carbon atoms per cluster. Here, we have used the above relation (eq. 4) to calculate the number of carbon atoms per cluster in irradiated PES.

Table I shows the comparison between the optical band gap energy and the size of the clusters for three different ion irradiated PES. From Table I, it is evident that the decrease in optical band gap with the increase in ion fluence for three different projectiles correspond to increase in cluster size. The cluster size varies from 98 to 159 Å, 98 to 224 Å, and 98 to 178 Å for proton, carbon, and neon ion irradiated PES.

It has been shown earlier for ion irradiated polymers⁴ that the correlation of normalized cluster sizes with the mean transferred electronic energy density (i.e., product of LET and ion fluence) gives a nearly universal correlation, in so far as differences in polymer species, projectile energies, and ion fluences cancel out. There is a faint dependence on projectile mass. The heavy projectiles are somewhat more efficient than the medium and light ions in cluster production because the mean transferred electronic energy density is about an order higher for the heavier Ne and C ions compared with that for proton.⁴ We have noticed the trend of the growth in the size of the clusters that was more for carbon and neon ion irradiated PES and less for proton irradiated PES.

Figure 4 shows the plot of the mean transferred electronic energy density versus the cluster size. The remarkable ion beam-induced cluster formation sets

in between 10^{-1} and $1 \text{ eV}/\text{Å}^3$ region. The plot shows the universal correlation, which is in agreement with the earlier reports.^{4,5} Besides the mean electron density, the mechanism of the energy distribution (deposition) is crucial in the ion-polymer interactions. To explain the energy deposition, the three required factors are as follows: (i) LET (stopping power), (ii) the ionization spatial distribution, and (iii) the stopping mechanisms.

In the aspect of radiation-induced chemical bond breaking and bond recombination, the heavier ions (Ne⁶⁺ and C⁺) are more efficient than the lighter one (H⁺). This is probably due to the following factors: (a) the heavier ion's stopping power (LET) is high, the generation of high density defects will also be more and that will have a larger chance to interact, producing irreversible recombinations; (b) the faster ions

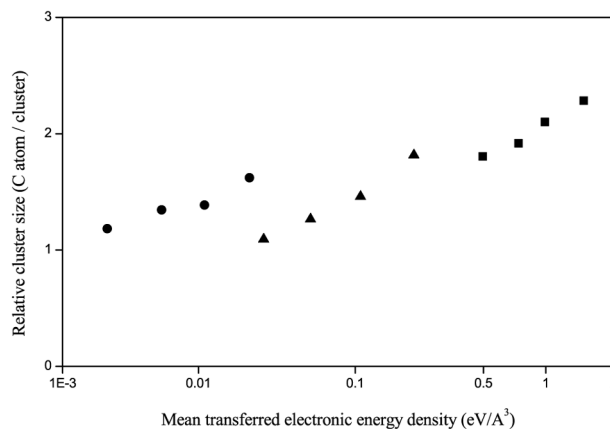


Figure 4 Normalized carbonaceous cluster sizes in irradiated polyethersulphone, as a function of mean electronic transferred energy density; (●) H⁺ ions irradiated; (■) C⁺ ions irradiated; (▲) Ne⁶⁺ ions irradiated.

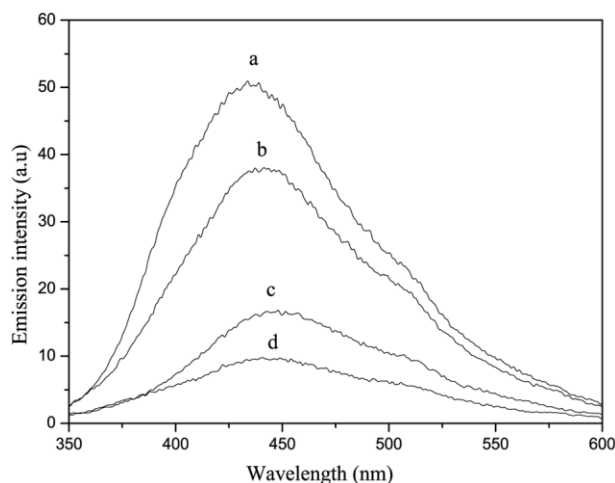


Figure 5 Fluorescence emission spectra of polyethersulphone irradiated with 4 MeV H^+ ions at different ion fluences; (a) 2×10^{13} ion/cm 2 ; (b) 5×10^{13} ion/cm 2 ; (c) 1×10^{14} ion/cm 2 ; (d) 2×10^{14} ion/cm 2 .

have smaller stopping power and the produced δ rays have a larger range and the resulting radical distribution is much wider.²⁷

Fluorescence spectroscopy

Fluorescence spectra of PES exhibit a broad peak at 440 nm when excited at 335 nm, which changes on irradiation with different ions at varied ion fluences. There was a sharp decrement in fluorescence emission intensity at 440 nm because of ion beam irradiation. In the case of proton-irradiated samples (Fig. 5), only the emission intensity decreases, with increase in ion fluence. But in the case of carbon and neon ion irradiated PES (Figs. 6 and 7), a new emission band appeared at 575 nm.

Ion Beam Induced Luminescence analysis is a sensitive technique to investigate the change in luminescence emission of the irradiated polymers. There are few reports that have used Ion Beam Induced Luminescence analysis,^{18,19} which also has good agreement with the spectrofluorimetric method.

Fluorescence emission spectra exhibit the growth of new luminescent structures in carbon and neon irradiated PES. The new luminescent band appeared at 575 nm (Figs. 6 and 7) and may be attributed to aggregates of phenyl radicals which is similar to hydrogenated amorphous carbon clusters.^{19,28,29} It has been found that amorphous carbon shows the same luminescent features, which is due to the recombination of electron-hole pairs in graphitic (π -bonded) clusters of hexagonal rings.³⁰ The heavier ions (C^+ and Ne^{6+}) that have high LET are more efficient to induce the bond breaking in the carbon skeleton, which is responsible for the luminescent feature, and to form

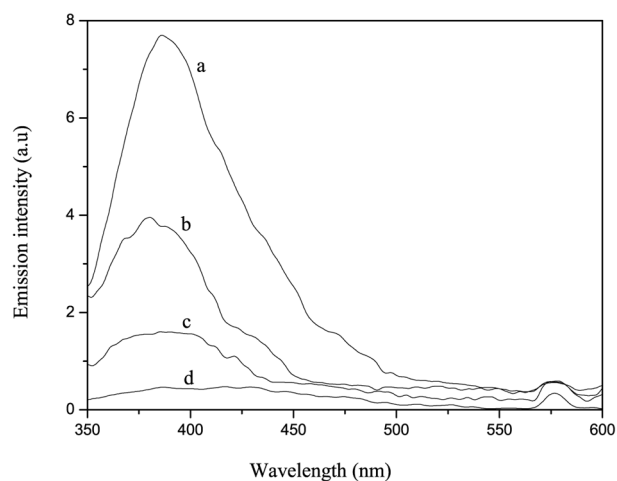


Figure 6 Fluorescence emission spectra of polyethersulphone irradiated with 3.6 MeV C^+ ions at different ion fluences; (a) 5×10^{13} ion/cm 2 ; (b) 7.5×10^{13} ion/cm 2 ; (c) 1×10^{14} ion/cm 2 ; (d) 1.5×10^{14} ion/cm 2 .

the amorphous carbonaceous cluster, which shows luminescent behavior. But, in the case of lighter ions (H^+), the efficiency to induce such changes is less. We have found that the average absorbed dose values were less in the case of lighter ions (H^+) and those values were higher for the heavier ions (C^+ and Ne^{6+}). The change in fluorescence intensity also depends on the average absorbed dose.

Fourier transform infrared spectroscopy

It is a sensitive tool to identify the chemical bond modification in the irradiated polymers. Figure 8

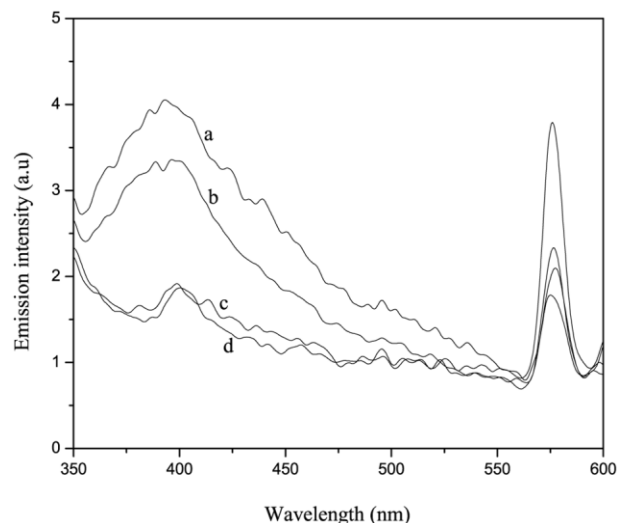


Figure 7 Fluorescence emission spectra of 145 MeV Ne^{6+} ion irradiated polyethersulphone at different ion fluences; (a) 4.22×10^{12} ion/cm 2 ; (b) 8.33×10^{12} ion/cm 2 ; (c) 1.66×10^{13} ion/cm 2 ; (d) 3.33×10^{13} ion/cm 2 .

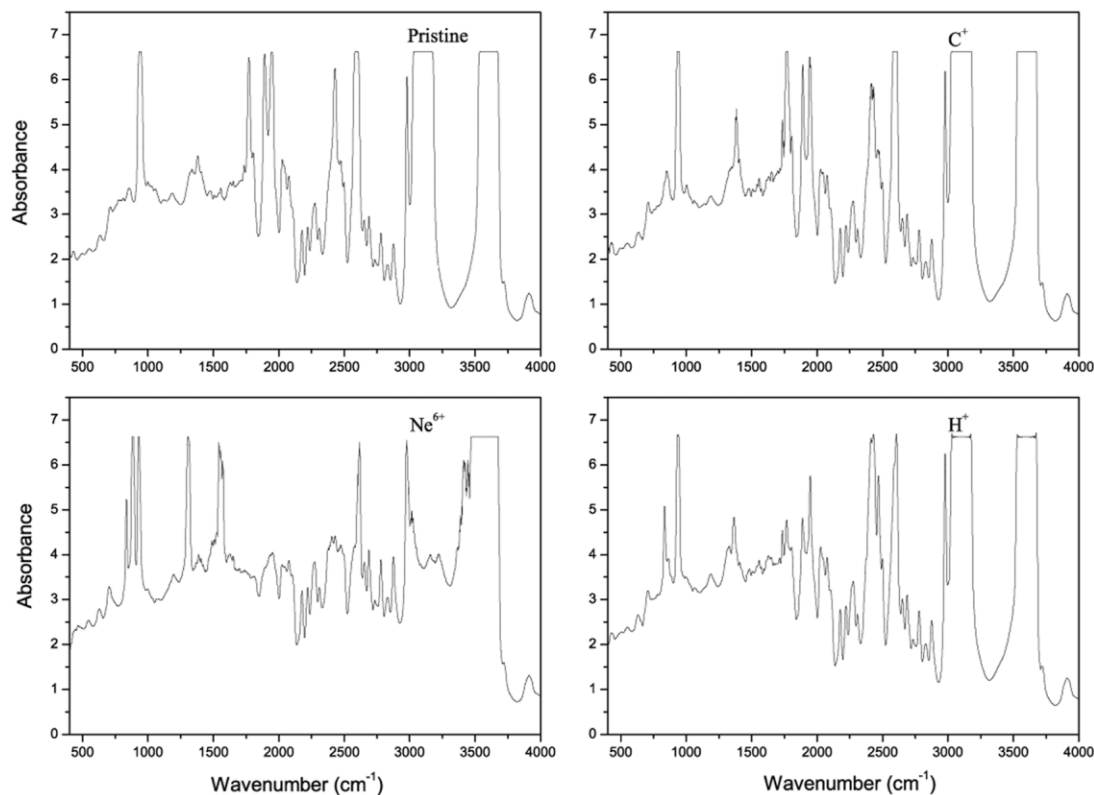


Figure 8 FTIR spectra of pristine, irradiated polyethersulphone with H^+ and C^+ ions at the ion fluence of 5×10^{13} ions/cm² and Ne^{6+} ions at the fluence 3.3×10^{13} ions/cm².

shows composite of FTIR absorbance spectra of pristine and proton, carbon, and neon irradiated PES at fluence of 5×10^{13} ions/cm². The FTIR spectra after irradiation show an overall reduction in the absorption of typical bands of pristine PES along with the formation of some new bands. It was found that the bands at 3050 cm^{-1} (CH stretching of aromatic ring), $2000\text{--}1660\text{ cm}^{-1}$ (overtone and combination of bands of aromatic ring), 1640 and 1562 cm^{-1} (aromatic ring stretching), and 708 cm^{-1} (CH out of plane bending) show reduction in absorption with different bombarding ions. The decrease in intensity of the sulfone absorptions at 1350 cm^{-1} (SO_2 antisymmetric stretching mode) and 1170 cm^{-1} (SO_2 symmetric stretching mode) were observed.

Irradiation with neon beam resulted in the formation of new bands at 3465 cm^{-1} , 3250 cm^{-1} that corresponding to the formation of O—H band and alkynes ($-C\equiv C-$), respectively (Fig. 8). The formation of alkynes was earlier reported in 5.6 MeV Sn irradiated polyethylene, polystyrene, poly(vinylidene fluoride),³¹ and in 8.6 MeV Kr irradiated poly(ethyleneterephthalate).³² However, in those systems, formation of alkynes groups was not found when irradiated with electron and carbon ion beam.³¹ It has been found that the average absorbed dose at the fluence of 3.33×10^{13} ions/cm² for the neon irradiated PES was

about 37 MGy and the mean electronic transferred energy density was about $2.152\text{ eV}/\text{\AA}^3$ whereas that for carbon irradiated PES was $0.496\text{ eV}/\text{\AA}^3$. The alkynes formation depends on the polymer structure and the threshold energy for the production. This indicates that the formation of triple bonds under irradiation is specific to high energy loss and insensitive to the chemical composition. Therefore, it requires a specific recombination of bonds and extreme high energy deposition. In the region of $800\text{--}900\text{ cm}^{-1}$, the additional spectral behavior indicates that there may be the formation of graphite-like structure as a result of radiation damage by neon ions.³³

CONCLUSIONS

The physicochemical modification of PES induced by 4 MeV H^+ , 3.6 MeV C^+ , and 145 MeV Ne^{6+} ions at different ion fluences has been observed. The gradual red shifting with the increase in absorption from UV to Visible region reveals the decrease in optical band gap, which results from the increase in cluster size. The heavier ions (C^+ and Ne^{6+}) are more effective to create such abovementioned changes than the lighter one (H^+). The significant decrement of fluorescence intensity with the increase in ion fluence has been noticed from the fluorescence emission spectra. In the

case of C^+ and Ne^{6+} irradiated PES, the formation of new luminescent band at 575 nm, being attributed to the amorphous carbon cluster, shows the efficiency of the heavy ions. For neon irradiated PES, significant chemical modifications occurred even at low ion fluence of 3.33×10^{13} ions/cm², corresponding to the average absorbed dose of about 37 MGy.

The authors thank the authority of Pelletron facilities of the Institute of Physics, Bhubaneswar, India, and Variable Energy Cyclotron Center, Kolkata, India, for providing them with the beam time for irradiation of the polymer samples. They also thank Prof. A. Datta and Ms. S. Chattopadhyay of Surface Physics Division of Saha Institute of Nuclear Physics for their help in recording FTIR measurements.

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