Influence of UV-Irradiation on Latent Tracks in Polyethylene Terephthalate Films *

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Polyethylene terephthalate (PET) films in thickness of 12 μm are irradiated by Xe and Au ions at the energies of 9.5 and 11.4 MeV/u and with the ion fluence from 5×10^9 cm^{-2} to 1×10^{11} cm^{-2}. After irradiation, ultra-violet lights are used to illuminate the samples with latent tracks at the wavelength of 365 nm with flux density of 4.2 mW/cm^{-2}. UV-irradiation effects on tracked PET are investigated by the UV-vis spectrum and positron annihilation lifetime spectroscopy (PALS). It is found that carbonaceous clusters in PET films are generated by ion irradiation and decomposed with UV illumination by calculating the optical energy band gap E_g in the UV-vis spectrum. The free volumes behave differently in track and bulk after UV illumination. In our experiment, the PALS results show an increase in radius and density of free volume in tracked PET films after UV treatment, which indicates an expansion in radius of latent tracks.

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Networks of defects or voids on the paths of swift heavy ions in dielectrics are called latent tracks. UV light illumination is known to be used as a common effective method to change the alkaline etching rate of the latent tracks in polymers.[1] It was found that after storage in the open air for a few weeks, the etching rate in tracked polymers increases significantly by oxidation.[2] Furthermore, exposure to UV light accelerates this process in polymers. After sensitization of tracks in polyethylene terephthalate (PET) by exposure to UV light for several hours, a high etching rate ratio could be achieved to fabricate nanopore with different pore diameters.[3] The nanopore in polymer film can undergo chemical modification with functional molecules, and can be subsequently built for biomimetic nanochannel systems.[4]

Numerous research studies have been carried out on the structure characteristics of the tracked PET films, while most of them can only provide the information of latent tracks on the surface.[5,6] Positron annihilation lifetime spectroscopy (PALS) is proved to be a powerful probe for the detection of atomic-scale free volume, which reflects porous properties of the sample.[7] The PALS results of lifetimes on polymer membranes with ion-irradiation at different fluences have been reported before.[8,9] Some other investigations, studying the chemical interaction between polymer films and UV light, show features consistent with a Norrish type-I based decarbonylation and a Norrish type-Ⅱ process producing terminal carboxylic acid groups.[10] However, the changes of inner structure and size of the latent tracks in polymer films during UV-illumination remain unclear. It is of great interest to see what happen in the nano-scale structure of the latent tracks in PET films.

Polymer films of polyethylene terephthalate (Hostaphan RN12, Hoechst, 12-μm-thick) were irradiated by swift heavy ions of Au with the energy of 11.4 MeV per nucleon at the UNILAC linear accelerator (GSI, Darmstadt, Germany) and Bi ions with the energy of 9.5 MeV per nucleon at heavy ion research facility in Lanzhou (HIRFL, China). All the irradiations were performed in a vacuum at room temperature, and a 30-μm-thick Al foil was placed in front of the samples in Bi ions irradiation experiment. Estimated in their mean values by SRIM,[11] the energy loss due to nuclear collisions would not exceed 10 eV/nm. Thus only electronic energy loss S_e (keV/nm) is considered in such high energetic ion irradiation. It was reported that if the deposited electronic energy loss exceeds 4.5 keV/nm a continuous and homogeneous cylindrical track core will be produced in most polymer materials.[12] Under our experimental conditions, the linear energy loss along the tracks in the polymer is about 14–17 keV/nm and is almost constant in the range of 12 μm (Fig. 1). The samples were kept in air for several weeks after heavy ion irradiation.

The UV irradiation was carried out at the wavelength of 365 nm, with a flux density of 4.2 mW/cm^2 for several hours on each side of the tracked PET films. The UV light is well-distributed enough to ensure that the fluctuation of light intensity is less than 5% over the surface of membranes under illumination.

The UV-vis spectrum was obtained by a UV-vis spectrophotometer (Hitachi uv-3010) in absorption mode in the wavelength of 800–200 nm at State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University.

The size and structure of the latent tracks were examined with positron annihilation lifetime spectra with a slow–fast coincidence system. A 16 μCi ^{22}Na positron source was used in the PALS measurement

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at the Institute of High Energy Physics (IHEP), CAS. Since the emission of the positron by the ^{22}Na source is only 3 ps later than the emission of a γ photon with the energy of 1.28 MeV, the accompanying photon captured by BaF_2 scintillation detector can be used as a 'start signal'. When the positron annihilates in the material, the released γ photon of 0.511 MeV is considered as a 'stop signal'. The time interval between the two signals is the lifetime of the positron. The signals were detected by a time spectrometer and were distinguished by different energies. Finally the positron annihilation lifetime spectrum was obtained by statistics of a large amount of events up to 2 million. Samples were stacked to 480 μm in thickness to make sure that signals were high enough to restrain the experimental error. The spectrum was resolved with the computer program Lifetime9.[13]

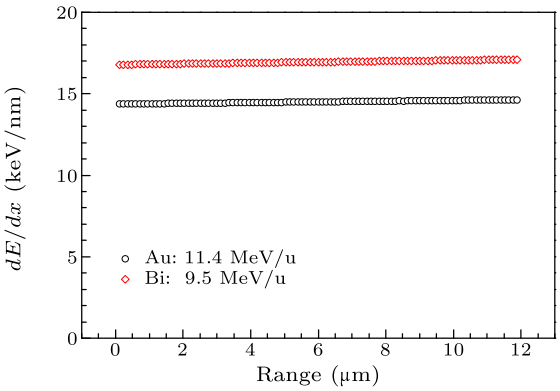


Fig. 1. SRIM calculated (electronic energy loss) for 9.5 MeV/u Bi and 11.4 MeV/u Au in PET samples.

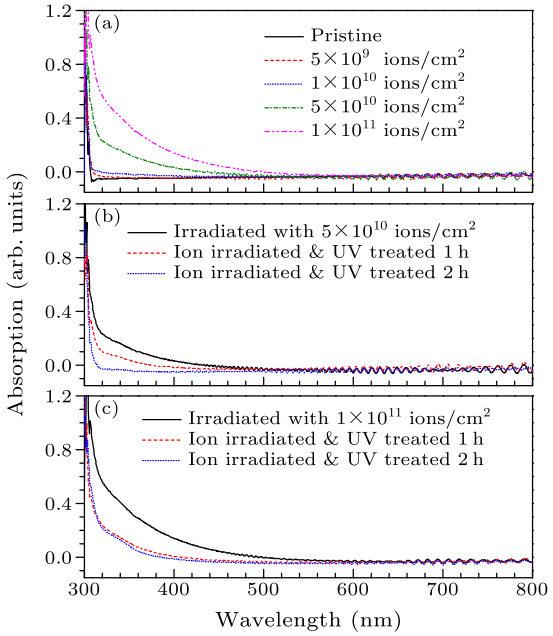


Fig. 2. Optical absorption versus wavelength for PET membranes irradiated by Bi of 9.5 MeV/u with (a) different fluences, (b) different UV treatment times at the same fluence of 5×10^{10} ion/cm^2, (c) different UV treatment times at the same fluence of 1×10^{11} ion/cm^2.

Previous research on the UV effect on pristine PET has been reported. CO and carboxylic acid production were found to be the major effects.[14] They were described by the Norrish type-I process based decarbonylation and Norrish type-Ⅱ process producing terminal carboxylic acid groups.

Actually, sensitization of the tracks in PET films by exposing to ultraviolet light before chemical etching has been a normal process for the fabrication of nanopore.[1] The relative higher etching rate led by this process is usually explained by assuming that the cross-linked structure of the polymer around the tracks is partially destroyed.[15]

The UV-vis spectroscopy suggests a strong increase in absorption with increasing the ion fluence (Fig. 2(a)). The increase may be attributed to the formation of a conjugated system of carbon bonds, as a consequence of bond breaking and reconstruction induced by irradiation.[16] UV-vis spectroscopy gives an idea about optical band gap E_g, which is an important tool to investigate bond structure in materials.[17] The optical band gap E_g of irradiated PET films could be calculated with the Tuac formula[18] from the UV-vis spectrum,

$$\alpha(\nu)h\nu = B_\alpha(h\nu - E_g)^2, \tag{1}$$

where B_α is a constant of disorder parameter, $\alpha(\nu)$ is the absorption coefficient at the frequency ν. The optical band gap can be calculated by plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$ and extrapolating the linear region of plot $(\alpha h\nu)^{1/2}$ to zero.

A structure of the network of an independent cluster of sp^2 bonded carbon atoms linked with sp^3 type sites was described in Robertson–O'Reilly's model.[19] The relation between optical band gap energy E_g and the number of hexagonal carbon rings in the cluster is given by

$$E_g = \frac{2|\beta|}{\sqrt{M}}, \tag{2}$$

where 2β is the band structure energy of a pair of adjacent π sites with the value of -5.8 eV,[20] and M is the number of hexagonal rings in a cluster. However, Fink *et al.* reported that the Robertson equation underestimates the cluster size in ion-irradiated polymers.[21] The structure of carbonaceous clusters should be assumed to be like a C_{60} ring instead of C_6, and the corrected relationship is

$$E_g = \frac{34.3}{\sqrt{N}}, \tag{3}$$

where N is the number of carbon atoms per cluster in samples. The calculated value of the band gap and the number of carbon atoms in carbon clusters are listed in Table 1.

From the calculation, it is found that the number of atoms in carbon clusters increases with the ion fluences, which could be explained that in the heavy ion irradiation process, carbonaceous clusters can be derived in carbonization in track cores, which is the most heavily damaged area.

After UV illumination, the optical absorption decreases with increasing the UV treatment time

(Figs. 2(b) and 2(c)). The increases of energy band E_g are attributed to the reduction of carbon atoms' number in carbonaceous clusters (Table 2). The clusters may be formed by sp^2 sites with free π orbitals that tend to agglomerate into a graphite bonded structure.[20] The structure is chemically active which could be photo-oxidated by UV light illumination and photo-decomposed to smaller fragments.

Moreover, the optical absorption in tracked PET films shows the saturation after exposure to UV light for hours (Fig. 2(c)) with increasing the ion fluences. For the ion fluence of $1 \times 10^{11}\,\mathrm{cm}^{-2}$, there is a significant decrease of absorption at the wavelength of 300–500 nm after UV treatment for 1 h, while after two-hour exposure to UV light, the values of absorption remain essentially unchanged. The result suggests that cross linking in tracks caused by overlapping at high ion fluence results in the stable structure against UV illumination.

Table 1. The variation of the band gap and the number of carbon atoms as a result of ion irradiation on PET films.

Fluence (cm^{-2})	Band gap (eV)	Number of carbon atoms (N)
Pristine	4.03	72
1×10^{10}	3.99	74
5×10^{10}	3.85	79
1×10^{11}	3.70	86

Table 2. The band gap and the number of carbon atoms as a result of UV illumination on PET films irradiated with different ion fluences.

Fluence (cm^{-2})	UV illumination time (h)	Band gap (eV)	Number of carbon atoms (N)
5×10^{10}	0	3.85	79
5×10^{10}	1	3.95	75
5×10^{10}	2	4.03	72
1×10^{11}	0	3.70	86
1×10^{11}	1	3.90	77
1×10^{11}	2	3.90	77

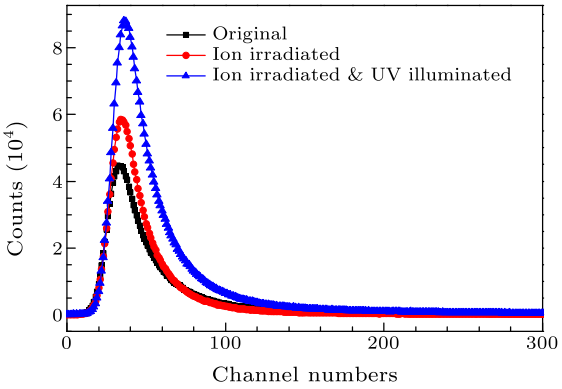


Fig. 3. Positron lifetime spectra of PET films with different treatments.

In the work of Vilensky *et al.*,[22] the appearance of new bands in the IR spectra was assigned to the carboxyl and carbonyl groups of the radiolysis products inside the tracks. It was also demonstrated that after UV-irradiation a rather large amount of products passed into water compared with the non-irradiated sample. The products were proven to decompose in water to terephthalic acid (TPA) according to the IR spectra.

Thus it can be proposed that the latent tracks are much more sensitive to ultraviolet light than the bulk materials in PET films. By the increase of the UV treatment time, the sensitization of tracks becomes weaker for the saturation of carboxyl groups and other oxidation groups.

The theory of free-volume suggests local positronium free volume as small holes. The probability of positronium formation increases with the amount of holes. Moreover, the larger the size of holes is, the lower their density is, thus the longer the lifetime of positronium is.[23] Position lifetime spectra of PET films with different treatments are given in Fig. 3. Three lifetime components are decomposed from the positron lifetime spectra, which arise from the annihilation of para-positronium (p-Ps, τ_1, 155–157 ps), free positron annihilation (τ_2, 300–400 ps) and ortho-positronium pick off process (o-Ps, τ_3, 1.5–3.5 ns). The long-living component τ_3 attributed to o-Ps pick off annihilation in free volume is sensitive to the structural changes in polymers.[8] However, considering that positrons annihilating in new groups can also influence the intensity of τ_3, we performed ATR-FTIR experiment (spotlight 200 infrared spectrometer, PE, USA) on the samples and proved that there is no detectable change in chemical groups between the PET films with ion irradiation and UV illumination.

Each of the lifetimes has a relative intensity, that is, I_1, I_2 and I_3, which is in proportion to probability of the appropriate process. The intensity of o-Ps (I_3) is related to the concentration of the free volume holes in polymers.[24] The relationship between the annihilation lifetime of pick-off ortho-positron (τ_3 in units of ns) and the radius of free volume can be described as a semi-empirical equation of model,[25,26]

$$\tau_3 = 0.5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}, \quad (4)$$

where ΔR is the thickness of electron layer that is around the free volumes and has an optimized value of 1.656 Å. It should be pointed out that a spherical model is used to simplify the simulation, as an approximation to the actual situation.

Table 1 lists the result obtained from o-Ps lifetime τ_3 for the values of the radius of the free volume hole and the volume of free holes V for the pristine PET film samples. The samples were irradiated with 9.5 MeV/u Au ions before and after UV-light treatment. The lifetimes and intensities of two short living components that are not shown in this table have com-

mon values for polymers: the lifetimes τ_1 and τ_2 are close to 0.15 ns and 0.4 ns, respectively.

It can be seen from Table 1 that the o-Ps lifetime τ_3 increases after heavy ion irradiation, so as radius R and mean value V of free volume holes. However, the intensity I_3 decreases first under ion irradiation, which indicates two competitive processes on free volumes occurring in the materials. To explain the results, we may consider the mechanisms of ion irradiation on polymers. Energetic ions' irradiation in polymers can cause cross linking as well as scission of chains, which depends essentially on polymer and track structure. Depending on the distance from the ion path, two regions are characterized: maximal polymer destruction and carbonization zone called track cores and radiation damage zone induced by electronic collision-cascade called the track halos. Ion irradiation modification in track cores with the size of several nanometers is predominantly chain scissions, while in track halos with the size up to 100–1000 nm it is predominantly cross linking.[27] Although chain scission leads to both reduction of mass and cross linking, it has been demonstrated that in track cores there is a large decrease of density due to the efficient release of gases,[28] as estimated from small angle x-ray scattering.[29] However, volumes of track halos are much larger than track cores, cross linking takes place in the vast majority of the region of material and thus reduces free volumes within original target materials. The two opposite effects finally cause the experimental results listed in Table 1, that after irradiation by swift heavy ions, intensity of free volume decreases due to the cross linking in the bulk materials. On the other hand, the radius of free volume increases for the creation of new free volumes in track cores that have larger sizes than those in the bulk.

The photo-oxidation and photodecomposition are supposed to happen in tracks with UV-irradiation: radiolysis products dissociate into small-molecular substances and generate gases such as CO_2 and CO, which could be released to air.[22] Thus free volumes in latent tracks expand as shown in the table that after UV treatment for 1 h, the PET films with the ion fluence of 5×10^9 have an increase in both radius and intensity of free volumes (I_3). The absorption of UV light in latent tracks is much stronger than that in the bulk material, and the influence of the bulk could be ignored.

Table 3. Lifetime parameters o-Ps, radius of free-volume hole and mean free volume in PET.

Ion dose (ions/cm^2)	UV time (h)	τ_3 (ns)	I_3(%)	R (Å)	V (Å^3)
Unirradiated	0	2.047±0.010	14.54±0.21	2.899±0.009	102.1±0.953
5×10^9	0	2.162±0.025	10.19±0.21	3.000±0.021	113.7±2.447
5×10^9	1	2.281±0. 022	13.11±0.19	3.101±0.018	124.9±2.209

In summary, UV irradiation effect on latent tracks in PET films has been studied by the positron annihilation technique and the UV-vis spectrum. The results indicate that the latent tracks are significantly affected by UV-light, while the bulk material does not display such a sensitization. The PALS results imply an expansion on the size of the latent tracks after UV treatment due to the generation of new free volumes induced by the release of gases and small photodecomposition products.

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References

[1] Benton E V and Henke R P 1969 *Nucl. Instrum. Methods* **70** 183
[2] Edmonds E A and Durrani S A 1979 *Nucl. Tracks* **3** 3
[3] Kalman E B, Vlassiouk I and Siwy Z S 2008 *Adv. Mater.* **20** 293
[4] Vlassiouk I and Siwy Z S 2007 *Nano Lett.* **7** 552
[5] Ohnesorge F M et al 2000 *Nucl. Instrum. Methods Phys. Res. Sect.* B **166–167** 938
[6] Apel P et al 1998 *Nucl. Instrum. Methods Phys. Res. Sect.* B **146** 468
[7] Mohamed H F M, Kobayashi Y, Kuroda S and Ohira A 2012 *Chem. Phys. Lett.* **544** 49
[8] Kumar R et al 2008 *Nucl. Instrum. Methods Phys. Res. Sect.* B **266** 1783
[9] Kumar R and Prasad R 2005 *Radiat. Meas.* **40** 750
[10] Zhu Z and Kelley M J 2005 *Polymer* **46** 8883
[11] Ziegler J F, Biersack J P and Littmark U 1985 *The Stopping and Range of Ions in Solids* (Oxford: Pergamon Press)
[12] Trautmann C, Bouffard S and Spohr R 1996 *Nucl. Instrum. Methods Phys. Res. Sect.* B **116** 429
[13] Kansy J 1996 *Nucl. Instrum. Methods Phys. Res. Sect.* A **374** 235
[14] Day M and Wiles M D 1971 *Polym. Lett.* **9** 665
[15] Vilensky A I and Tolstikhina A L 1999 *Russ. Chem. Bull.* **48** 1100
[16] Kumar R et al 2006 *Nucl. Instrum. Methods Phys. Res. Sect.* B **251** 163
[17] Mishra R et al 2000 *Nucl. Instrum. Methods Phys. Res. Sect.* B **168** 59
[18] Tauc J, Grigorovici R and Vancu A 1966 *Phys. Status Solidi* **15** 627
[19] Robertson J and O'Reilly E P 1987 *Phys. Rev.* B **35** 2946
[20] Awasthietal K et al 2010 *Radiat. Meas.* **45** 850
[21] Fink D et al 1996 *Nucl. Instrum. Methods Phys. Res. Sect.* B **111** 303
[22] Vilensky A I et al 2003 *Radiat. Meas.* **36** 131
[23] Brandt W, Berko S and Walder W 1960 *Phys. Rev.* **120** 1289
[24] Shantarovich V P 1996 *J. Radioanal. Nucl. Chem.* **210** 357
[25] Tao S J 1972 *J. Chem. Phys.* **56** 5499
[26] Jean Y C 1990 *Microchem. J.* **42** 72
[27] Apel P et al 1997 *Nucl. Instrum. Methods Phys. Res. Sect.* B **131** 55
[28] Picq V et al 1998 *Nucl. Instrum. Methods Phys. Res. Sect.* B **146** 496
[29] Albrecht D et al 1985 *Appl. Phys.* A **37** 37