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(Citation)

Radiation detectors and their uses (KEK Proceedings), 2010(10):1-11

(Issue Date)

2010-12

(Resource Type)

conference paper

(Version)

Version of Record

(URL)

<https://hdl.handle.net/20.500.14094/90005411>



ON THE TRACKS OF PROTON AND HEAVY IONS IN PC AND PADC PLASTICS DETECTORS

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In order to understand the latent track formation mechanics in polymeric nuclear track detectors, chemical modification along heavy ion tracks in bisphenol A polycarbonate, PC, and poly(allyl diglycol carbonate), PADC, has been examined using Fourier transform infrared, FT-IR, spectrometry. Track core radius for loss of carbonyl has different dependence on the stopping power between PC and PADC, indicating a quite different response to heavy ions from each others. This implies a possibility of controlling the track registration characteristics by changing the molecule structure between two carbonate ester bonds. In PC, the tracks have three different regions. The central region lost all three functional groups of carbonate ester bonds, phenyl rings and methyl groups, which surrounded by the second region in which the carbonate ester bonds and phenyl rings were damaged. In the outer region, the carbonate ester bonds were lost.

1. INTRODUCTION

This study intends to understand the chemical modification along ion tracks in bisphenol A polycarbonate, PC, and poly(allyl diglycol carbonate), PADC, films by means of Fourier transform infrared, FT-IR, spectrometry, which are well known materials as Etched Track Detectors. Both materials contain a common function group that plays an important role during the chemical etching, in which the attacking by the hydroxide ions in alkaline solution caused the hydrolysis of the carbonate ester bonds. PADC is confirmed to have higher track registration sensitivity than PC. Such difference in the sensitivity has could be discussed in the comparison on each radio-sensitivity of molecule parts between the carbonate ester bonds. FT-IR

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spectrometry is a suited method to estimate the kinds and amounts of function groups composing polymeric materials. Many important studies in the field of radiation chemistry have been carried out for variety types of polymers⁽¹⁻³⁾, including etched track detectors, ETDs, like a cellulose nitrate film⁽⁴⁻⁶⁾.

There has been an increasing interest for the irradiation effects on PC, that is an important engineering plastic with optical clarity, high impact strength, heat stability, water resistance, high percent elongation and so on. It is a candidate material for a track membrane, which could be templates for nano-tubes and nano-wires manufacturing⁽⁷⁾. As classical radiations, the irradiation effects of UV on PC has been well reviewed by Rivaton⁽⁸⁾, and that of gamma ray was summarized by Factor et al⁽⁹⁾. Several types of free radicals induced in PC have been identified by ESR spectrometry, which was exposed to gamma ray or heavy ions^(10, 11). A small-angle X ray scattering study was also applied for U ion track core in PC⁽¹²⁾. The radial damage distribution in heavy ion tracks has been examined by the electrolytic cell method⁽¹³⁻¹⁶⁾ and Transmission Electron Microscope, TEM, observations on the replica of the minute etch pits^(17, 18), evaluating the transversal track etching rate. Lots of FT-IR studies on PC exposed to heavy ions have been performed⁽¹⁹⁻²⁹⁾. Nevertheless only a few quantitative analyses have been made, including the estimation of the radiation chemical yield or G value. Amorphization around heavy ion tracks were confirmed by X-Ray Diffraction, XRD, analyses^(24, 25, 28). These works are quite useful to understand some feature of latent tracks in PC, but not all of they were conducted from the viewpoint of studies on ETDs.

We have applied three different methods to estimate the track core size in PADC. In the UV-method, the core size was evaluated from the fluence dependence of UV-visible spectra of ion irradiated PADC films, based on the track overlapping model⁽³⁰⁻³⁴⁾. Evolution of minute etch pits on PADC during the early stage of chemical etching has been observed by mean of Atomic Force Microscope. The trends of etch pit growth behavior provided us the core size where the radial track etching rate was enhanced (AFM-method)⁽³³⁻³⁵⁾. FT-IR studies have been also performed for PADC films exposed to heavy ions, which gives us information on chemical modification along tracks as well as track core size (IR-method)⁽³⁶⁻⁴⁰⁾. Several studies have been made using FT-IR spectrometry by many authors^(19, 20, 41-46). The PADC samples were too thick to obtain unsaturated IR spectra, which is inevitable to analyze the spectra quantitatively based on the Beer-Lambert law. A small-angle neutron scattering study was carried out for proton irradiated PADC⁽⁴⁷⁾. Free radicals induced in PADC has been examined using ESR spectrometry⁽⁴⁸⁾. The electrolytic cell method was applied for proton irradiated PADC films⁽⁴⁹⁾. Number of studies has been limited on the latent tracks in PADC compared to that on PC films.

In the present study, chemical modification along heavy ion tracks in PC and PADC has been studied by means of FT-IR spectrometry. For PC, the damage density for the loss of carbonyl bonds, phenyl rings and methyl bonds per unit length of tracks were assessed for He, C, Ne, Ar, Fe, Kr and Xe ions, as a function of stopping power. The G values and the corresponding effective track core radii for each group were also evaluated. On the carbonate ester bonds, the results are compared with that from PADC. The latent tracks in PC has three different zones. The center lost all three functional groups, which was surrounded by the second zone in which the carbonate ester bonds and phenyl rings were damaged. The outer zone lost only the carbonate ester bonds. Breaking of more than two neighbor carbonate ester bonds

would produce the latent tracks, which are able to be developed by following chemical etching.

2. EXPERIMENTS

Figure 1 is a scheme of PC, which has phenyl rings, methyl groups and a carbonate ester bond. Commercially obtained PC films with an average thickness of 3 μm (Makrofol KG, Goodfellow) were utilized throughout this study. It was made as stacks of about 15 films during heavy ion exposure, in which incident ions can be stopped completely. Figure 2 shows a repeat unit of PADC polymer network. It contains two carbonate ester bonds at symmetric positions from the center of ether bond via ethylene. Sufficiently thin films of PADC with about 2 μm thick were prepared by chemical etching starting from 100 μm thick sheet of BARYOTRAK (Fukuvi Chemical Ltd. Japan), which made from purified monomer more than 99.9%. Heavy ion exposures were performed on each PADC film without stacking.

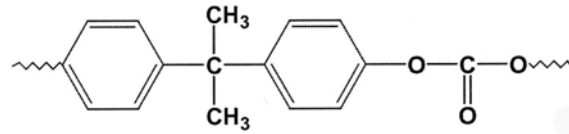


Fig. 1 Repeat unit of PC.

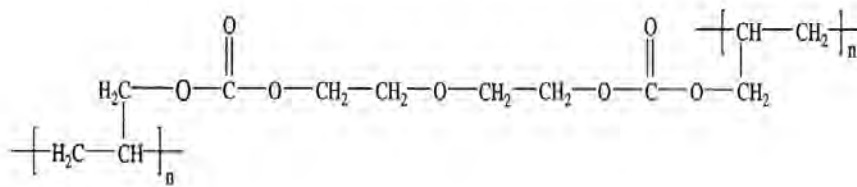


Fig. 2 Repeat unit of PADC.

Proton and heavy ion irradiations were performed in air at the port of the medium energy irradiation room of HIMAC, NIRS, Japan. Incident ion energies on the samples of PC stacks and PADC films are as listed in table 1. FT-IR measurements were performed for each film both before and after the irradiation using FT/IR6100S (JASCO, Japan), the entire system of which was evacuated, including the interferometer, photon-detector, and sample room, during the measurements, in order to avoid the influence of moisture and carbon dioxide in air.

Table 1 Incident energy on the sample surface (MeV).

	H	He	C	Ne	Ar	Fe	Kr	Xe
PC	---	20	28	47	103	137	207	208
PADC	5.7	20	25/58	24	46	147	220	200

3. RESULTS AND DISCUSSION

3.1 Radiation damage on carbonyl in PC

Figure 3 indicates IR spectra of PC film before and after 24 MeV Ne ions irradiation with a fluence of 1.2×10^{11} ions/cm². The intensities of indicating absorption peaks of methyl groups,

phenyl-rings and carbonate ester bonds, C=O and C-O-C, are decreased due to the exposure. Figure 4 shows the fluence dependence of relative absorbance, A/A_0 , which is the ratio of net absorbance of carbonyl after the irradiation, A , to the original one, A_0 , for three PC films in different depth in the stack. Indicating ID number starts from the top surface of the stacks and the film No. 8 located at the Bragg peak. We found the observed trends were expressed well by the following experimental formula as a function of ion fluence, F , in a unit of ions/cm² for films in each depth,

$$A/A_0 = 1 - \sigma_i \cdot F, \quad (1)$$

where σ_i is an experimental constant for ID number of i in units of cm². This constant means the effective track core cross-section in which carbonyl bonds were lost. In the region of fluences where the overlapping of tracks was negligible, the relative absorbance is equivalent to the survival fraction of carbonyl bond, N/N_0 , that is the ratio of density on the bond after the irradiation, N , to that of original density, N_0 , in a unit of bonds/cm³. The product of σ_i by N_0 is the damage density, L , number of loss of carbonyl per unit length of the track as like,

$$L = \sigma_i N_0. \quad (2)$$

Depth distribution of the damage density is shown in Fig. 5, as well as the calculated stopping power by SRIM code⁽⁵⁰⁾. In this figure L is given in a unit of bonds/μm. Correlation between the damage density and the averaged stopping power in each film for all heavy ions examined is shown in Fig. 6. The best fitting curve indicated the damage density is almost proportional to the averaged stopping power. The G value for loss of carbonyl bonds in PC per 100 eV was attained from the ratio of the damage density to the averaged stopping power. Figure 7 indicates the G value for heavy ions, showing slight dependence on the stopping power. This implies that the increasing stopping power resulted in the increasing the number density of the identical radiation damage. Slightly smaller value of 1.3 was reported as the values of CO and CO₂ formation, which correspond to loss of carbonate ester bond, for PC exposed to gamma ray⁽⁹⁾. Track core radius for loss of carbonyl, $r_{C=O}$, was also derived from the values of σ_i , under the simple relation, i.e. $\sigma_i = \pi r_{C=O}^2$. The result is plotting in Fig. 8 as a function of the stopping power. We obtained the following experimental formula in a form of power function:

$$r_{C=O} = 0.041(-dE/dx)^{0.53}, \quad (3)$$

where $r_{C=O}$ is in a unit of nm and the stopping power is in keV/μm.

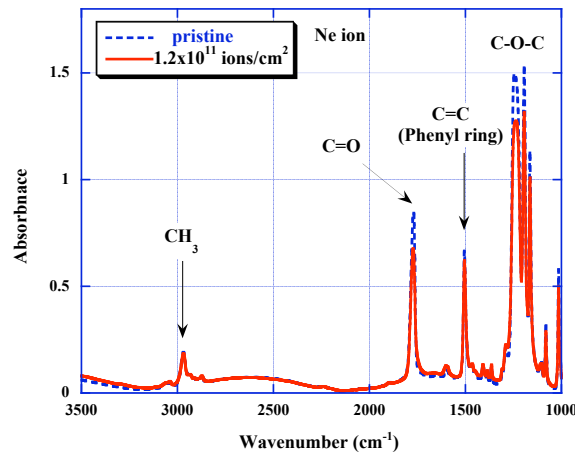


Fig. 3 IR spectra of pristine and irradiated PC with 24 MeV Ne ions.

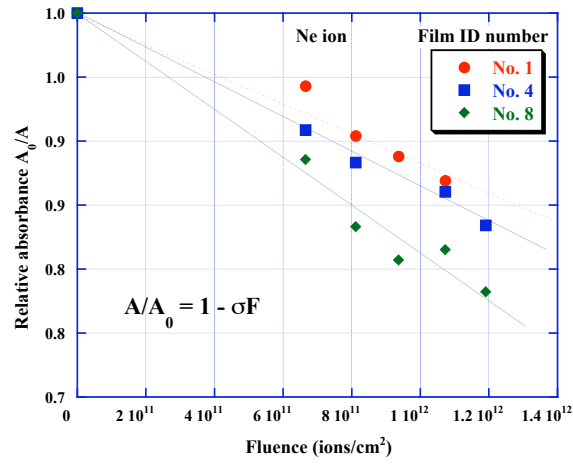


Fig. 4 Decrease of relative absorbance for carbonyl in PC with fluence of Ne ions.

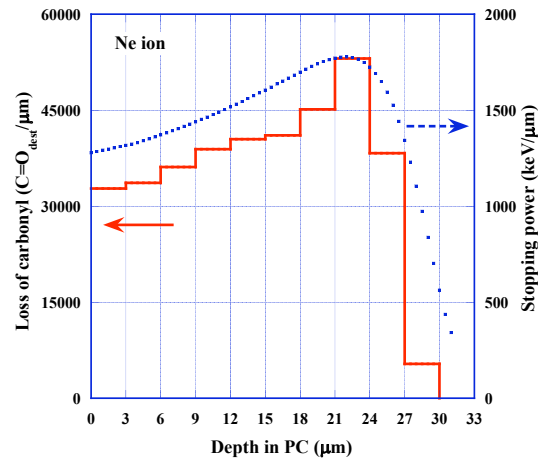


Fig. 5 Depth dependence of damage density in PC exposed to Ne ions.

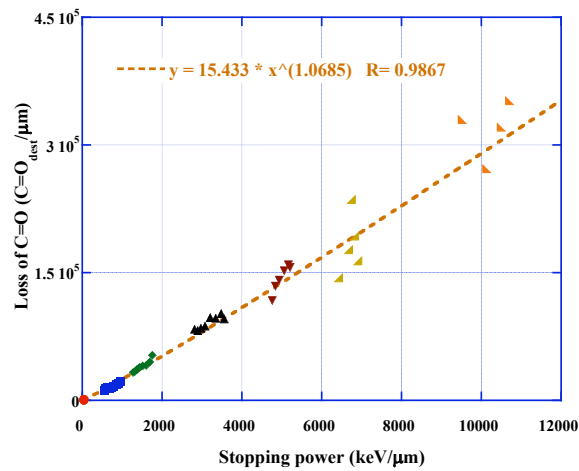


Fig. 6 Correlation between the damage density and the stopping power.

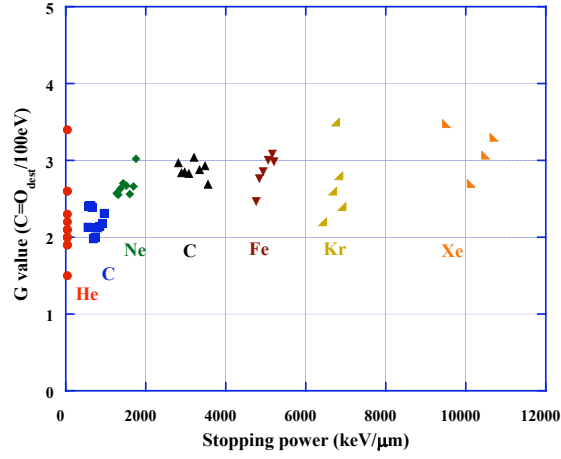


Fig. 7 G value of loss of carbonyl in PC for heavy ions.

The track core radius is found to be almost proportional to the square root of the stopping power. It should be noteworthy to be pointed that the core radius will be exactly proportional to the root of stopping power, when the G value has no dependence on the stopping power.

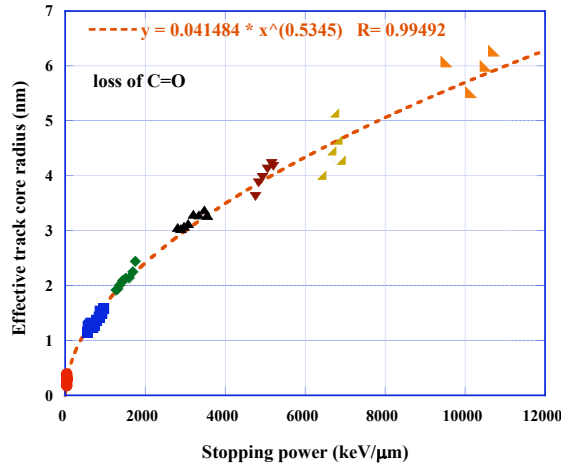


Fig. 8 Effective track core radius for loss of carbonyl in PC.

3.2 Radiation damage on carbonyl in PADC

Similar experiments have been made for PADC films exposed to proton and heavy ions⁽³⁶⁻⁴⁰⁾. We have found the chemical damage parameters, like the damage density, G value and track core radius, have different dependence on the stopping power between the lower stopping power region less than about 1000 keV/μm and the higher region. Figure 9 shows the track core radius for the loss of carbonyl bond in PADC against the stopping power. The experimental formula in a type of power functions are as followings, for the lower region:

$$r_{C=O} = 0.17(-dE/dx)^{0.32}, \quad (4)$$

and for higher region:

$$r_{C=O} = 0.015(-dE/dx)^{0.67}. \quad (5)$$

where $r_{C=O}$ is in nm.

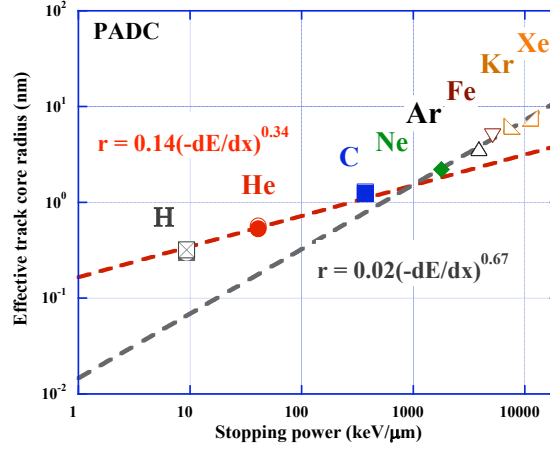


Fig. 9 Effective track core radius for loss of carbonyl in PADC.

3.3 Effects on phenyl-ring and methyl group in PC

Series of IR measurements and analyses have been performed for phenyl-ring and methyl group in PC. Effective track core radii for the loss of them are shown in Fig. 10 against the stopping power. Equations 6 and 7 are the experimental formulas,

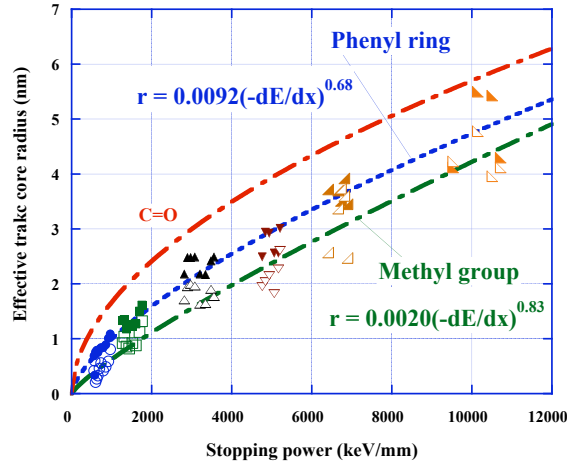


Fig. 10 Effective track core radius for loss of phenyl-ring and methyl group in PC.

$$r_{P-ring} = 0.0092(-dE/dx)^{0.68}, \quad (6)$$

$$r_{CH_3} = 0.0020(-dE/dx)^{0.83}, \quad (7)$$

where r_{P-ring} and r_{CH_3} are in nm. This figure and the relations apparently indicate that the heavy ion tracks in PC have three different zones. The first central zone lost all three functional groups, which was surrounded by the second zone where the carbonyl and phenyl rings were damaged. The third outer zone lost only the carbonyl bonds. Since PC has track registration sensitivity for low energy He ions above 100 keV/μm, the core size is about 0.8 nm almost equal to the length of PC repeat unit. This means the breaking of more than two neighboring carbonate ester bonds should be key-phenomena producing the latent tracks, which will be developed by following chemical etching. Higher G values for loss of phenyl and methyl groups

are a result of the multi breaking of carbonate ester bonds in the neighborhood (Fig. 11).

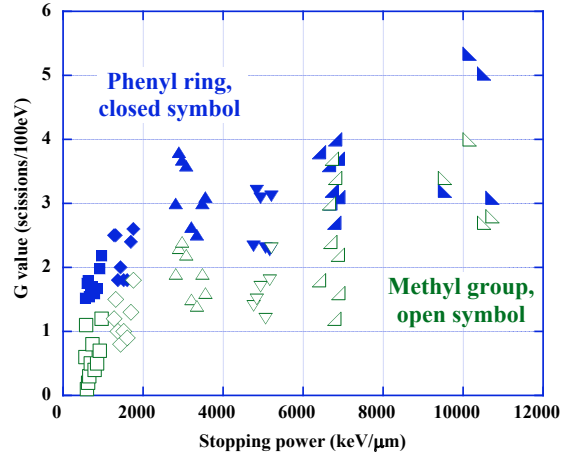


Fig. 11 G value of loss of phenyl and methyl groups in PC for heavy ions.

4. CONCLUSION

Chemical modification along heavy ion tracks in PC and PADC has been examined using FT-IR spectrometry. Track core radius for loss of carbonyl has different dependence on the stopping power between PC and PADC. This means the carbonate ester bonds show quite different response to heavy ions in PC and PADC. This can be important information to find more sensitive ETD materials. In PC, the tracks have at least three regions. The central region lost all three functional groups of carbonate ester bonds, phenyl rings and methyl groups, which was surrounded by the second region in which the carbonate ester bonds and phenyl rings were damaged. The outer region lost only the carbonate ester bond that is the most sensitive for radiations. General trends are shown in Fig. 12 as the three solid lines. Each experimentally attained formula for track core radius of loss of the three functional groups is concordant to the other FT-IR studies including U ion^(23, 24).

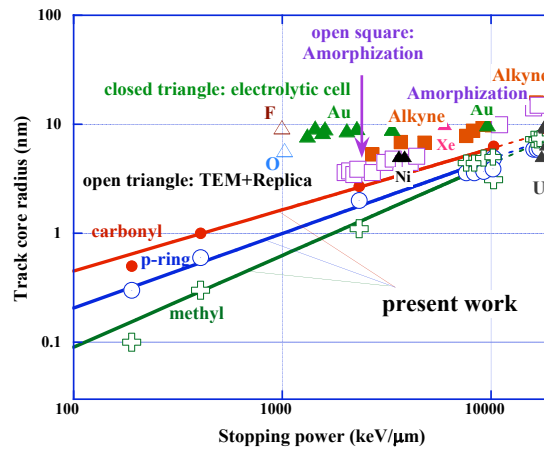


Fig. 12 Track core radius in PC by different methods .

Closing the present study, we would review briefly the relating studies on the track halo or penumbra in PC. Track radii from XRD studies have larger values as shown in Fig. 12, as

well as that from formation of alkyne by FT-IR^(24, 25). Amorphous structure containing alkyne bonds will be produced in the track halo surrounding the track core with lower density, losing the carbonate ester bonds and others. It is also found that electrolytic cell method⁽¹³⁻¹⁶⁾ and TEM study on the replica of etched track^(17, 18) give much larger value for the track radius. The region with significantly higher radial track etch rate should be larger than the amorphous or the alkyne containing regions. Similar trend was found for tracks in PADC, in comparing the results from AFM-method and UV-method⁽³³⁻³⁵⁾.

Acknowledgements

We would like to express our thanks to the staff of NIRS-HIMAC for their support during the experiments (p138). This work was carried out as a part of the Research Project with Heavy Ions at NIRS-HIMAC. We wish to thank Dr. Teruaki Konishi in the experiments using HIMAC. We would like to express our heartfelt thanks to Mr. S. Watanabe for his efforts during the experiments in his Master Course. We are much indebted to Mr. Atsushi Sakamoto, Mr. Hiraku Chikada, Mr. Yusuke Maeda, Mr. Masato Kanasaki in the experiments.

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