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Radiation chemical yield for loss of carbonate ester bonds in PADC films exposed to gamma ray

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Abstract

Radiation chemical yield, G value, for loss of carbonate ester bonds in PADC films, exposed to gamma ray from intense Co-60 source, has been determined by means of FT-IR spectrometry. The obtained value of 20 (scissions/100 eV) is fairly higher than that from heavy ion irradiations. It was found the density of hydroxide group in the film significantly increased by the exposure in air but hardly changed in vacuum.

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Keywords: PADC; CR-39; Gamma ray; G value

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1. Introduction

In our recent studies, a series of FT-IR measurements has been carried out for PADC, poly(allyl diglycol carbonate) , films exposed to heavy ions, in order to clarify the radial size and chemical structure of the latent tracks (Yamauchi et al., 2008a&b). We found dependence of G value, i.e., radiation chemical yield, on the stopping power of heavy ions. These findings have been discussed based on the radial dose distribution theory (Waligórski et al., 1986). These results should be compared with the effect of gamma-irradiation on PADC, to understand the unique energy deposition process in spatial and temporal aspects along nuclear tracks.

O'Sullivan et al. inferred G value of gamma ray scissions in PADC per 100 eV as higher than 10, from the correlation between the minimum value of primary ionization rate and the G values for various kinds of polymers based on the observed bulk etching rates (1981). Unfortunately, no radiological study about PADC track detector followed their work, while several studies have been done for other types of polycarbonate (Factor et al., 1994). Among nuclear track detectors, the G value of gamma ray has been reported for LR-115 films, demonstrating the effectiveness of FT-IR spectrometry (Barillon and Yamauchi, 2003).

In the present study, G value for loss of carbonate ester bonds in PADC films has been determined by FT-IR spectrometry, which are exposed to gamma ray in air from an intense Co-60 source. Obtained results are compared with those from heavy ions irradiations. The out-gassing effect in vacuum of PADC film is also reported.

2. Experimental

PADC films used in this work were obtained by chemical etching of BARYOTRAK with a nominal thickness of 100 μm (Fukuvi Chemical Industry Co., Ltd., Japan), which was made from the purified monomer. The detail of the thinning process has been described elsewhere (Yamauchi et al., 2008a&b). Following the etchings the samples, typically with thicknesses from 2 to 3 μm, were rinsed in distilled water carefully and then dried in a clean and dark space after blowing out the excess water on the surface.

Samples were exposed to a gamma ray field generated by an intense Co-60 source of the Institute for Scientific and Industrial Research, Osaka University (370 TBq at the end of March 2000). During the exposure, each film was sandwiched by PMMA sheets with 2 mm thick to achieve the electron equilibrium condition. The total

absorbed dose ranged from 300 kGy to 1 MGy at a constant dose rate of 1.25 Gy/s. Another sample was kept in an evacuated quartz-glass tube below 10^{-4} Pa about one week before the exposure. The gamma-irradiation was made with a dose of 1 MGy at the same distance from the source as the other samples, inside the quartz-glass tube sealed by a connecting metallic valve. After the exposure the tube was evacuated again below 10^{-4} Pa for one week, prior to the air leak for the following FT-IR measurements. This was made to avoid some possible oxidative reactions of long living radicals in the irradiated PADC film (Böhlke and Hermsdorf, 2008).

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. The thickness of each film was precisely determined by the IR absorbance of typical bands based on the calibration curves (Yamauchi et al., 2008a).

3. Results and discussion

Figure 1 shows IR spectra of PADC film with a thickness of 3.2 μm before and after the gamma-irradiation with a dose of about 1 MGy. It is apparent that the absorption bands observed at 1250 cm^{-1} and 1770 cm^{-1} decrease in height due to the exposure, which are assigned to C-O-C and C=O, respectively, composing the carbonate ester bonds. The broad peak appeared around 3500 cm^{-1} indicates the formation of OH groups by the exposure.

The relative absorbance, A/A_0, was attained for each examined absorbed dose, where A is the net absorbance of the considering band after the exposure and A_0 is that of original one. According to the definition, the relative absorbance is equal to the survival fraction, N/N_0, which is the ratio of the number density of the considering chemical bond, N, to that of original, N_0. Namely, $A/A_0 = N/N_0$. Figure 2 shows the results for both C=O and C-O-C bonds, presenting the linear decrease of the relative absorbance against the absorbed dose for the both up to about 800 kGy. We obtained the following simple experimental formula:

$$N/N_0 = 1 - k_i \cdot D, \qquad (1)$$

where D is the absorbed dose in a unit of Gy and k_i is an experimental constant for the bond i in Gy^{-1}. The constant k_i is corresponding to the slope of the fitting lines in Fig. 2. They are easily converted to G values for the loss of C-O-C and C=O bonds per 100 eV, utilizing the following simple relation:

$$G = 9.64 \times 10^6 N_0 k_i , \quad (2)$$

where N_0 is in mol/kg. N_0 is 7.30 mol/kg for the carbonate ester bond in PADC. The calculations led G values of 21.6 and 19.8 for C-O-C and C=O bonds, respectively. As a result, G value for the loss of carbonate ester bonds in PADC is determined to be 20.

Figure 3 shows IR spectra of PADC irradiated by gamma ray in vacuum with a dose of about 1 MGy. The thickness of the film was 2.2 μm. As shown in this figure, absorption bands of C-O-C and C=O decrease clearly in height by the exposure at the almost same efficiency to that exposed in air (see Fig. 1). The G value was hardly affected by the vacuum condition. On the other hand, the yield of OH group formation is quite low compared to the case of the irradiation in air, as represented in Fig. 1. The loss of the carbonate ester bonds should be a result of a radio-physics process, while the OH groups should be produced by radiation-induced oxidization processes, consuming oxygen from the atmosphere (Yamauchi et al., 2003). This implies the suppression of OH group formation is what we call the vacuum effect.

The obtained G value can be compared to that from heavy ions irradiations (Yamauchi et al., 2008b). In Fig. 4, the G values for C, Ne, Ar and Fe ions with incident energies of 25, 24, 46 and 147 MeV, respectively, are presenting as a function of the averaged stopping power in the films, as well as the present value for gamma ray with *LET* of 0.4 keV/μm. It is apparent that the carbonate ester bonds in PADC are more effectively destroyed by gamma-irradiations compared to the heavy ions irradiations. Because of the huge energy deposition, breaking of the almost all kinds of bonds would become possible locally along the heavy ion tracks. As a result relatively small G values were derived for heavy ions, in which we measured the density of carbonate ester bond only.

4. Closing remarks

The radiation chemical yield, i.e., G value, has been determined to be 20 per 100 eV for the loss of carbonate ester bonds in PADC track detector exposed to gamma ray. The yield hardly affected by the vacuum condition. The formation of OH group was found to a result of radiation-induced oxidization processes consuming oxygen from the atmosphere. The present G value for gamma ray is fairly higher than that previously obtained from the heavy ion irradiations.

We are working now to evaluate the yield for other kinds of heavy ion and protons, paying attention also to different function groups, for example, ether and

ethylene, in order to understand all aspects what occur in PADC exposed to ionizing radiations. We think this kind of fundamental research will be inevitable and helpful to find new materials for SSNTDs.

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Figure Captions

Figure 1 FT-IR spectra of 3.2 μm PADC film before and after the gamma-irradiation with a dose of 1 MGy.

Figure 2 Decrease of relative absorbance for C-O-C and C=O bands with gamma dose. The examined doses are 319, 638, 846 and 1002 kGy.

Figure 3 FT-IR spectra of 2.2 μm PADC film before and after the gamma-irradiation in vacuum with a dose of 1 MGy.

Figure 4 G values for the loss of carbonate ester bonds with the averaged stopping power in PADC films for heavy ions (Yamauchi et al., 2008b) and that of gamma ray at *LET* of 0.4 keV/μm. The values of solid symbols were estimated from C=O and the open ones from C-O-C bonds.

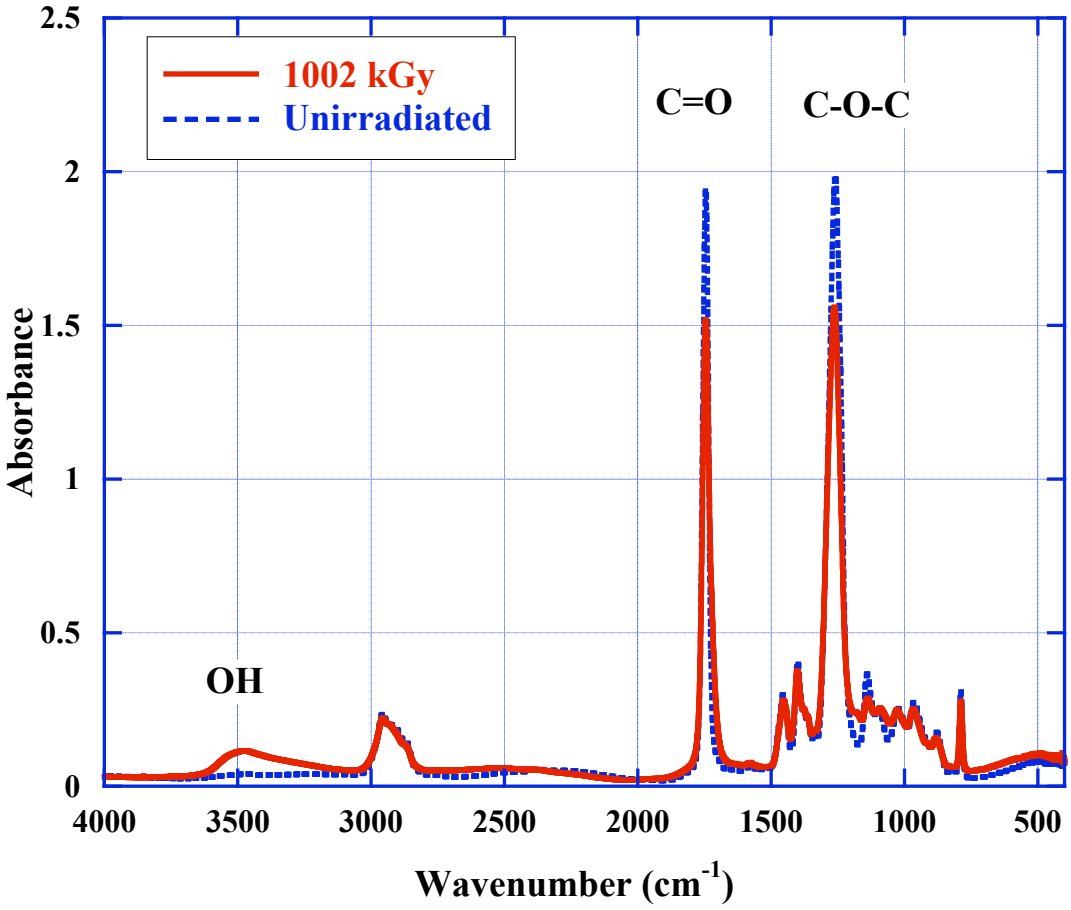
1002 kGy
Unirradiated
C=O
C-O-C
OH
Absorbance
Wavenumber (cm-1)
2.5
2
1.5
1
0.5
0
4000
3500
3000
2500
2000
1500
1000
500

Fig. 1

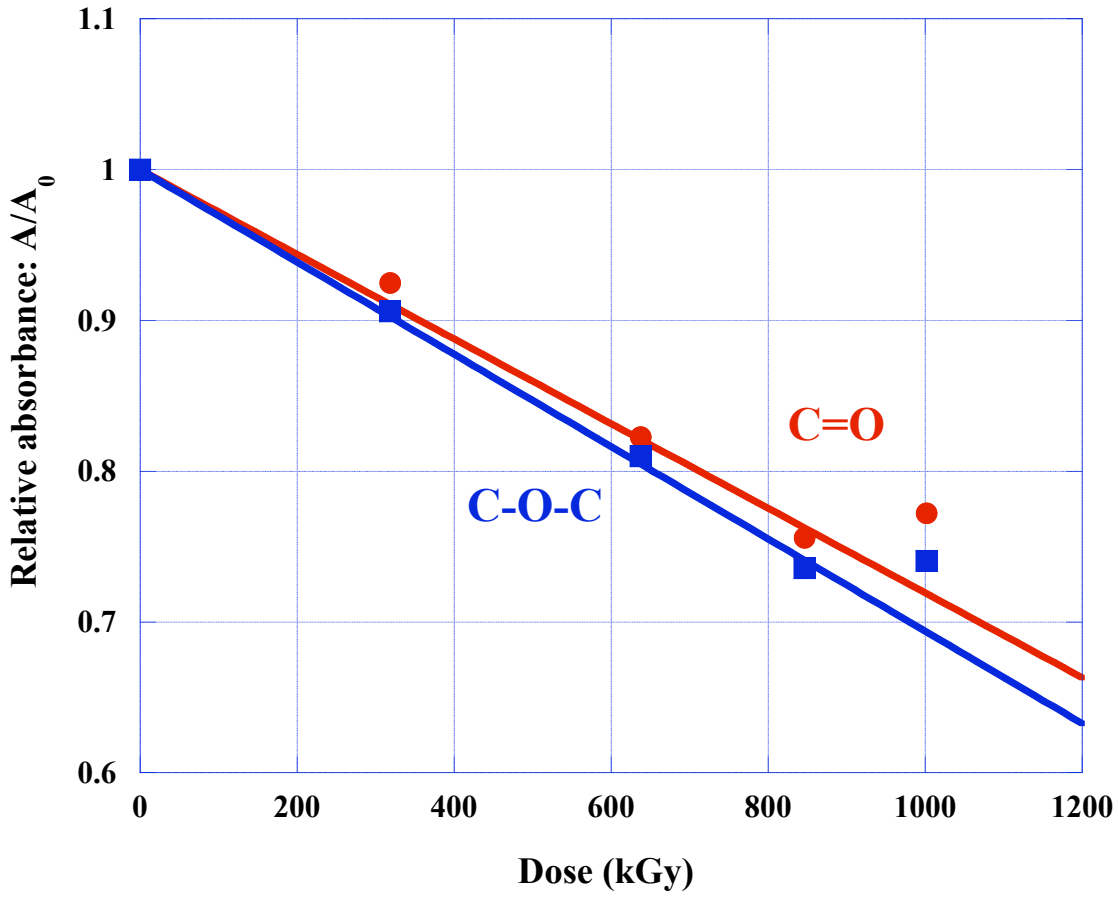
1.1
1
0.9
0.8
0.7
0.6
Relative absorbance: A/A0
0
200
400
600
800
1000
1200
Dose (kGy)
C=O
C-O-C

Fig. 2

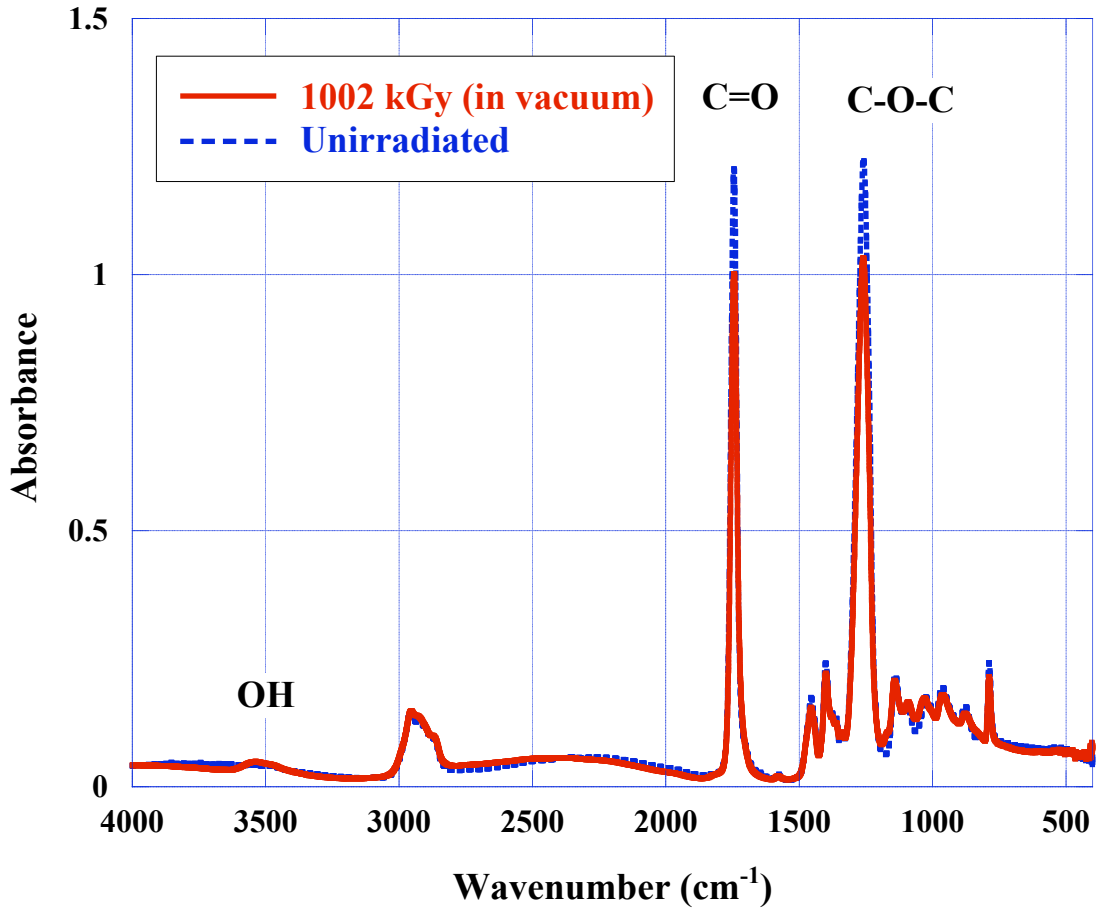
1.5
1
0.5
0
Absorbance
1002 kGy (in vacuum)
Unirradiated
C=O
C-O-C
OH
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Fig. 3

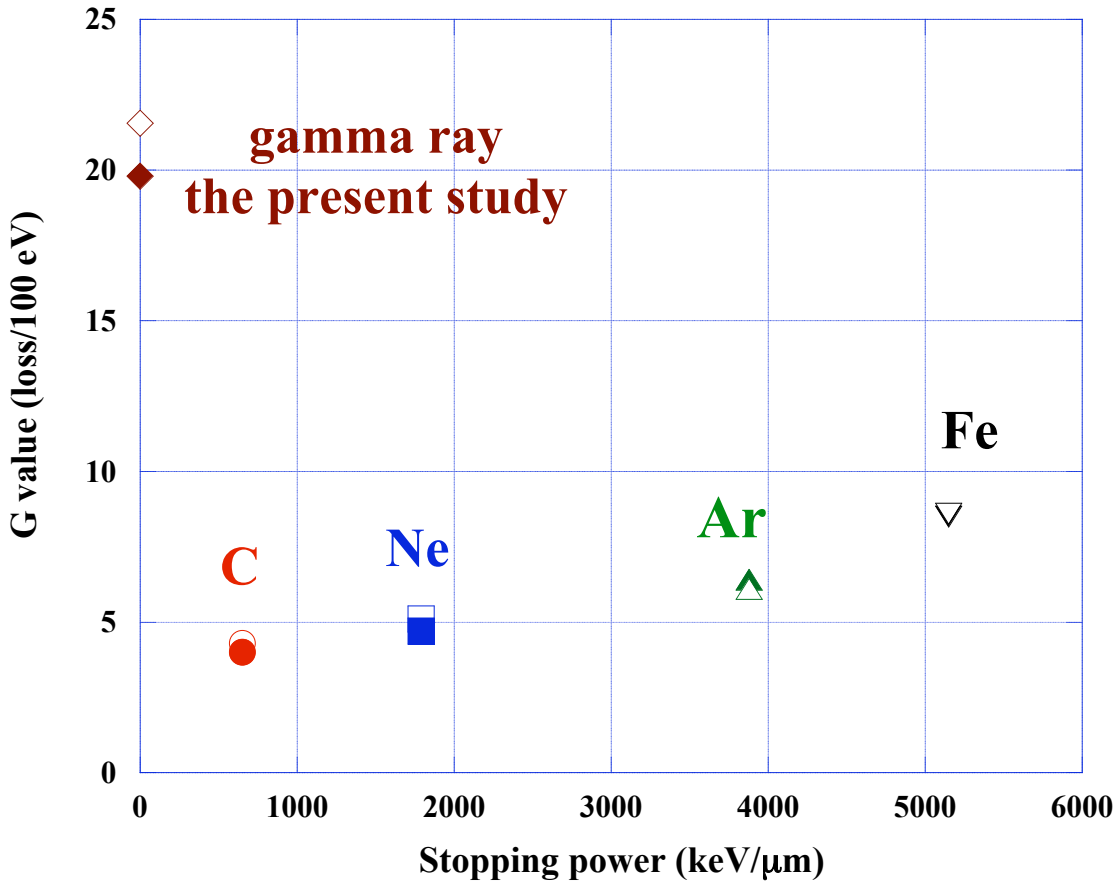
25
20
15
10
5
0
G value (loss/100 eV)
gamma ray
the present study
C
Ne
Ar
Fe
0
1000
2000
3000
4000
5000
6000
Stopping power (keV/μm)

Fig. 4