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Vacuum effects on the radiation chemical yields in PADC films exposed to gamma rays and heavy ions

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HIGHLIGHTS

- Characteristics of tracks in PADC formed after vacuum irradiations are examined.
- *G* values are not sensitive for irradiation environment for He and C ions.
- *G* value for gamma ray in vacuum is about half of that in air.
- Generated OH groups should be the damage which enhance track etch rate.

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ABSTRACT

In order to understand the vacuum effects on the sensitivity of PADC detectors from the viewpoint of molecule structural modification along nuclear tracks, a series of FT-IR spectrometric studies has been made for PADC films exposed to He and C ions at energies below 6 MeV/n, as well as to gamma rays from an intense Co-60 source, under the both conditions of in air and in vacuum. The radiation chemical yields for the losses of ether and carbonate ester bonds are hardly affected by the environmental conditions in the cases of He and C ion irradiations. For gamma ray, the yields are about half in vacuum compared to those in air. The formation of OH groups is fairly suppressed in vacuum in all cases. Recombination of free radicals resulted in modified polymeric network formation would be enhanced in heavy ion irradiations rather than in that of gamma irradiations.

1. Introduction

More than 30 years have passed since the discovery of Poly(allyl diglycol carbonate) (PADC) plastics as a sensitive etched track detector (Cartwright et al., 1978). Applications of this detector have been widely spread up to now, but there are still unresolved aspects on the track formation process in this material (Yamauchi, 2003). One of the unresolved issues is the vacuum effect on the sensitivity. It became to be well known that the track registration sensitivity decreases as oxygen pressure decreases in the environment (Somogyi, 1981; Barwick et al., 1983; Drach et al., 1987; Csige et al., 1991; Fujii et al., 1987, 1997). Fujii et al. found that the reaction between radiation-induced radicals and dissolved oxygen plays an important role in the formation of the etchable tracks in PADC (Fujii et al., 1987). It is interpreted to be a result of highly ionizing particles breaking polymer bonds, leaving free radicals that either react with free oxygen dissolved in the polymer to form a permanent latent track which is etchable, or failing to form a latent track, recombine, depending on the concentration of oxygen along the particle's trajectory (Drach et al., 1987). Using this model, Yamauchi et al. examined in detail track registration in PADC detectors outgassed in vacuum, and attained two components of radicals with a lifetime of about 40 min and a few minutes (Yamauchi et al., 1992). A numerical calculation has been done for dissolved oxygen and the damage distributions in depth direction of PADC detectors during gamma irradiations (Yamauchi et al., 2003b),

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based on the comprehensive etching studies after exposure to low *LET* radiations, gamma ray and high energy electron beams (Oda et al., 1997; Yamauchi et al., 1999, 2001a,b). The effects of oxygen on the track formation in PADC detectors was recently reviewed by Dörschel et al. and it was suggested that this effect strongly depends on both restricted energy loss and depth in the detector (Dörschel et al., 2005). More recently, a relating study using Fe ions with 110 MeV/n has been performed (Kodaira et al., 2009). But little study has been performed on the modified chemical structure around the latent tracks formed in PADC under the vacuum conditions.

We have been conducting FT-IR studies on the latent tracks of proton and heavy ions in PADC, as well as on the radiation damage caused by gamma ray in it, reporting some chemical damage parameters, like the radiation chemical yields, *G* values, for the losses of ether and carbonate ester bonds, the corresponding track core radius, in which the considering chemical function group is lost, and the damage density along the tracks, which is defined as the loss number of the considering chemical bonds per unit length of the ion tracks (Mori et al., 2009, 2011; Yamauchi et al., 2003a, 2005, 2008a,b). Most of these studies have been made after the irradiation in air. In this study, the chemical modification along ion tracks in PADC films has been studied by means of FT-IR spectrometry, which were exposed to He and C ions in vacuum, as well as to gamma rays from an intense Co-60 source. Results are carefully compared to that from the present and previous experiments in air for these ionizing radiations. For heavy ions, the damage density, track core radius and the *G* value are evaluated for each ion. The *G* values are also assessed for gamma ray. It has been confirmed that OH groups were formed in PADC network as newly produced end points, which is the permanent damage tightly related to the enhancement of the both bulk and track etch rates. Formation of OH groups is suppressed in vacuum. The *G* values for the losses of ether and carbonate ester bonds are hardly affected by the irradiation conditions for He and C ions, whether it was performed in air or in vacuum.

2. Experimental

Throughout this study, thin PADC films prepared by chemical etchings in KOH solution were used. Starting with commercially obtained PADC sheets of BARYOTRAK with a nominal thickness of 100 μm, it was reduced in thickness down to below 3 μm. Such thin films allows us to attain unsaturated IR absorption spectra including peaks for carbonate ester bond that has the strongest absorption in chemical function groups in PADC polymer structure. Fig. 1 shows a repeat unit of PADC, which has an ether bond in the center and two carbonate ester bonds in symmetric positions. These parts are radio-sensitive, easily breaking at C–O bonds after the exposure (Yamauchi et al., 2003a, 2005, 2012). Each repeat unit combines to polyethylene like polymer chains at the both ends, which were made from the polymerization of PADC monomers. These parts are relatively radiation tolerance, constructing the three dimensional general frame of this material.

Heavy ion irradiations, with He and C ions, were performed at the port of the medium energy irradiation room of Heavy Ion Medical Accelerator in Chiba, HIMAC, NIRS, Japan (Konishi et al., 2005; Yasuda et al., 2005). A special vacuum chamber was utilized, which has its own Havar foil for the beam introduction. Heavy ion beams once go out to air via the Havar foil of the beam port and enter the vacuum chamber passing through the thin air layer and the Havar foil of the chamber. We can control the pressure in the chamber independently to that of the beam line, as well as parallel uses of the beam port for other exposure experiments in air. Samples were set on a revolving sample holder. Before the irradiations the samples were kept in vacuum below 10^{-4} Pa for 2 days. Irradiation conditions of incident energies and fluencies were summarized in Table 1. The indicating stopping power is the averaged ones in films using SRIM code (Ziegler, 2004). After the irradiation samples were kept in vacuum for more than 1 day and then kept in sealed chamber for more than 30 days to avoid possible reaction with long life radicals and oxygen in air (Böhlke and Hermsdorf, 2008; Yamauchi et al., 1992).

Gamma irradiation was performed with an intense Co-60 source of the Institute for Scientific and Industrial Research, Osaka University (370 TBq at the end of March 2000). PADC films were sandwiched by PMMA sheets with 2 mm thick to achieve the electron equilibrium condition (Oda et al., 1997; Yamauchi et al., 1999, 2001a,b). The sample sets were kept in an evacuated quartz-glass tube, which has a metallic valve, below 10^{-4} Pa about 1 week before the exposure. The exposure to gamma ray was performed by putting the quartz-glass tubes after firmly seal the valve. The total absorbed doses ranged from 400 kGy to 1 MGy, at a constant dose rate of about 1.0 Gy/s. After the exposure, the quartz-tube was evacuated below 10^{-4} Pa for more than 1 week, prior to the FT-IR measurements (Mori et al., 2009).

The FT-IR measurements were made for each film both before and after the irradiation using FT/IR-6100S (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.

3. Results and discussion

3.1. Losses of ether and carbonate ester bonds in vacuum

Fig. 2 shows IR spectra of a PADC film with a thickness of 2.0 μm before and after the exposure to 48 MeV C ions at a fluence of 2.4×10^{10} ions/cm^2 in vacuum. The dotted curve indicates the spectrum of the pristine film and the solid curve is that of exposed one. Two strong absorption peaks at 1250 and 1770 cm^{-1} are assigned to C=O and C–O–C bonds, respectively, which compose carbonate ester bonds (Darraud et al., 1994; Lounis-Mokrani et al., 2003). These are clearly deceased in height due to the exposure. The peaks of ether bonds are observed at 1024, 1094 and 1140 cm^{-1} (Darraud et al., 1994; Lounis-Mokrani et al., 2003). We conducted the following quantitative analyses paying the attention on the peak at 1024 cm^{-1} for the ether bond, which is fairly isolated from other peaks among the three. It is apparent that the absorption bands for the ether also decrease in height after the exposure. This means that the ether and carbonate ester bonds are reduced in the density along ion tracks formed in vacuum. As a comparison, IR spectra of a PADC film irradiated by C ions in air are shown in Fig. 3.

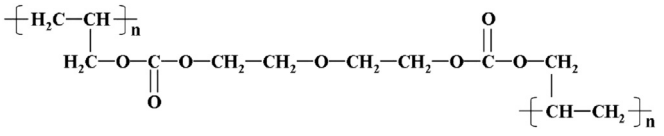

Fig. 1. A repeat unit of PADC.

Table 1
Irradiation conditions of heavy ions.

Ion	Incident energy (MeV)	Stopping power (keV/μm)	Fluence (ions/cm^2)
He	21.8	38	7.4×10^{12}–1.5×10^{13}
C	48.2	430	2.4×10^{12}–4.4×10^{12}