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Yields on the formation of OH groups and the loss of CH groups along nuclear tracks in PADC films

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HIGHLIGHTS

- Effective track core radius for the loss of CH groups is obtained in PADC.
- The CH groups are lost in the center region of the track core with other functional groups.
- The molar absorption coefficient for OH of water absorbed in PADC is obtained.
- The density of OH groups in PADC is comparable to the damage density of ether bonds.

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ABSTRACT

Modified structure along ion tracks in poly(allyl diglycol carbonate), PADC, films exposed to protons and heavy ions, He, C, Ne, Ar, Fe, and Xe, in air has been examined by means of FT-IR spectroscopy, covering the stopping power ranging from 10 to 12,000 keV/μm. The damage density for the loss of CH groups and the amount of formed OH groups along each tracks are estimated and compared to the previous results on the ether and the carbonate ester bonds. The CH groups are lost in the center region of the track core with other functional groups and the OH groups are created as new end-points of the polymer network. We obtained the molar absorption coefficient for OH of water absorbed in PADC films as 9.7×10^3 M^{-1} cm^{-1}. It has been assumed that the coefficient is applicable to the OH groups on the polymer. The amount of OH groups are almost equivalent to the damage density of the ether bonds.

1. Introduction

Since poly(allyl diglycol carbonate), PADC, has been known as the most sensitive etched track detector, it is important to understand the latent track structure to develop new detectors with higher sensitivity. We have conducted a series of FT-IR studies on PADC films exposed to gamma rays, protons and heavy ions in this decade (Mori et al., 2009, 2011, 2013; Yamauchi, 2003; Yamauchi et al., 2008a, 2008b). Formation of CO_2 gas and OH groups were confirmed after the irradiations (Yamauchi et al., 2003a, 2005). The losing behavior of ether and carbonate ester bonds along tracks were examined quantitatively as a function of the stopping power. CO_2 gas is produced by destructing the carbonate ester bonds. The ether is the most radio-sensitive part in PADC network. To well-describe in more details the track and to have a holistic view on the tracks, we must understand the behavior of CH groups which are sandwiched by such radio-sensitive parts. In addition, no attempt have been made to assess the amount of OH groups formed along the tracks in PADC. The present study intends at evaluating the damage density of CH groups and the amount of OH groups in PADC films exposed to protons and heavy ions in air. In order to assess the amount of OH groups, molar absorption coefficient of OH groups of water absorbed in PADC films was determined and applied, based on the specially designed experiments on the mass of water absorbed in the films.

2. Experimental

Two kinds of PADC films with different thickness were prepared

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as samples, starting with BARYOTRAK (Fukuvi Chemical Industry Co., Ltd., Japan) with a nominal thickness of 100 μm, which was made from the well purified monomer. To obtain the totally unsaturated IR spectra, we have reduced the thickness to below 3 μm by the chemical etching in KOH solution. In evaluating the density of OH groups in PADC, as well as the amount of absorbed water, we utilized the films with a thickness of about 12 μm. The detail of the thinning process was described elsewhere (Yamauchi et al., 2008b). The PADC films were exposed to protons and heavy ions (He, C, Ne, Ar, Fe, Xe) in air at Heavy Ion Medical Accelerator in Chiba, HIMAC, NIRS, Japan. Irradiation conditions of incident energies and the stopping powers were given in Table 1. The stopping powers are averaged values in each film, calculated by SRIM code (Ziegler, 2004). FT-IR measurements were performed for each film both before and after the irradiation using FT/IR-6100S (JASCO, Japan), the entire system which can be operated in vacuum, including the interferometer, photon-detector, and sample room, during the measurements. This made it possible to measure the absorbance of OH groups formed on PADC network, avoiding the influence of the absorbed water. In order to determine the amount of water absorbed in PADC films, we used the Karl Fischer Coulometric Titrator which connects to the Evaporator with the maximum temperature of 300 ° of C (EV-2000 and AQ-2200, Hiranuma Sangyo Co., Ltd., Japan). The detection limit is 10 μg of water. The Electronic analytical scale was also used to determine the mass of water (AG245, METTLER TOLEDO, Japan).

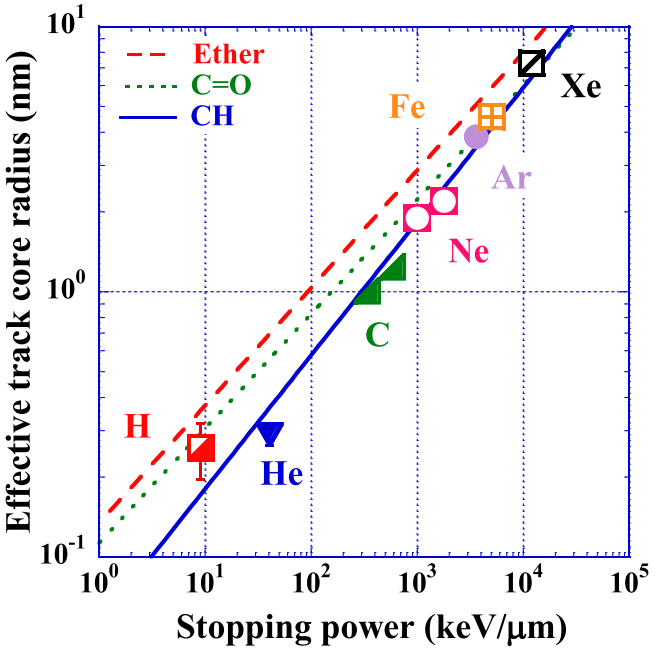

Fig. 1. Effective track core radii for the losses of ether, carbonyl and the CH groups against the stopping power.

3. Results and discussion

3.1. Losses of CH groups

FT-IR spectroscopy is a suitable method to examine irradiation effects on polymers (Balanzat et al., 1995; Barillon and Yamauhi, 2003; Dehaye et al., 2003). IR spectra of PADC also have been studied by many authors (Darraud et al., 1994; Gagnadre et al., 1993; Lounis-Mokrani et al., 2003). In this study, we focused on the peak of rolling CH at 789 cm^{-1} which is clearly isolated. Similar to the other functional groups like the ether and the carbonate ester, the absorbance of CH group was reduced after the irradiations (Mori et al., 2011, 2012, 2013). From the dependence of the absorbance to the fluence, we have obtained the removal cross sections for each ion as shown in Table 1 including the statistical errors. We obtained the track core radius from the removal cross sections as shown in Fig. 1. The solid line is the fitted trend. The core radius increases almost monotonically with the stopping power. The broken line and the dotted line are the trends of core radii for the losses of the ether and the carbonate ester bonds, respectively. CH groups are less radiosensitive than those two other groups.

3.2. Formation of OH groups

As shown in the inset of Fig. 2 there are three IR peaks around 3600 cm^{-1}, the first one is assigned as the anti-symmetric vibration of water (3635 cm^{-1}), the second is the symmetric vibration of water and OH groups in the polymer (3550 cm^{-1}), and the third is the first overtone of the carbonyl bond (3470 cm^{-1}) (Malek and Chong, 2000). These spectra show the drying process of PADC films in air which was stored in water (Yamauchi et al., 2003b). We repeated the FT-IR measurements and the mass measurements to follow the drying process and obtained the correlation between the mass of water and the absorbance as shown in Fig. 2. The absorbance was assessed from the difference spectra where the saturation level was set as the base. The Karl Fischer method was also applied to PADC sheets with different thicknesses between 10 and 50 μm. Through these experiments, we derived the molar absorption coefficient of OH for water absorbed in PADC film as $\varepsilon = 9.7 \times 10^3$ M^{-1} cm^{-1}. In the following, we assumed that the newly formed OH group on the PADC network have the identical molar absorption coefficient to this. So we derived amount of OH per unit distance of track length by the following equation:

$$\Delta C = (A - A_0)/\varepsilon l \quad (1)$$

where ΔC is the change of molar concentration, A_0 is the absorbance of original one, A is the absorbance of after irradiation and l is the thickness of sample. Since the maximum reduction rate of

Table 1
Summary of irradiation conditions of protons and heavy ions, removal cross section and amount of OH.

Ion	Incident energy (MeV)	Stopping power (keV/μm)	σ (cm^2)	Amount of OH (OH/nm)
H	5.7	9.2	$(2.08 \pm 0.87) \times 10^{-15}$	3.08
He	20	41	$(2.65 \pm 0.47) \times 10^{-15}$	7.12
C	25.2	640	$(4.84 \pm 0.13) \times 10^{-14}$	–
	58.8	370	$(3.18 \pm 0.20) \times 10^{-14}$	33.4
Ne	24.2	1800	$(1.52 \pm 0.08) \times 10^{-13}$	–
	82.7	1000	$(1.13 \pm 0.09) \times 10^{-13}$	74.0
Ar	59.9	3600	$(4.66 \pm 0.40) \times 10^{-13}$	292
Fe	145.6	5100	$(6.54 \pm 0.49) \times 10^{-13}$	489
Xe	303.6	12,000	$(1.66 \pm 0.13) \times 10^{-12}$	1820