Chapter 26

Application of Polyaniline Films to Radiation Dosimetry

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Radiation-induced doping of polyaniline was applied to a measurement of the integrated radiation dose. Samples consisting of undoped polyaniline and polyvinylchloride powder were irradiated with ^{60}Co γ-rays. The conductivity increased along with an increase in the dose in the range of 10 to 10^5Gy. It was shown that this method in the polyaniline system is promising for radiation dosimetry. The relationship between the amount of doped chlorine and the conductivity increase of polyaniline is discussed.

Conducting polymers have been expected to be applied to various electrical devices and sensors. In this work, radiation-induced doping was applied to the measuremet of the integrated radiation dose in a polyaniline system. It has been reported that radiation results in an increase in the electrical conductivity of conducting polymers due to radiation-induced doping in electron irradiation for polyacetylene (*1, 2*) and polythiophene (*3–5*) and in neutron irradiation for polyacetylene (*6*). Yoshino et al. (*3, 7*) have pointed out that radiation-induced doping can be applied to measurements of radiation in a polythiophene–SF_6 system.

In high-energy accelerator facilities, the beam-line components are exposed to high radiation fields. A device for measuring the integrated radiation dose is very important in estimating the radiation damage of these accelerator components. Such devices are required to be highly stable to radiation and to have the capability of measuring a very wide range of doses. Polyaniline is known to exhibit a drastic increase in its conductivity, by about 10 orders of magnitude, by doping it with a protonic acid (*8*). A polyaniline device using the radiation-induced doping technique is therefore one of the candidates for dosimeters used in such facilities.

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The prepared polyaniline samples consisted of a strip of an undoped polyaniline and the source material of the dopant, which were sealed in a glass-ampoule *in vacuo*. Halogenated materials were used as the source material, from which gases formed through radiolysis were supplied. The halogen-containing dopant gas reacts with the film on its surface. This radiation-induced doping results in an increase in its surface conductivity.

It is considered that the increase in electrical conductivity can be expressed as a function of the concentration of the dopant absorbed on the surface. The amount of dopant depends on the G-value of the dopant gas liberated from the source material, the weight of the source material and the integrated radiation dose. Therefore, the relationship between these parameters and conductivities must be elucidated in order to apply this method as a radiation dosimeter.

This paper reports on the characteristics of a polyaniline sample consisting of a polyaniline strip and polyvinylchloride (PVC) powder, while focusing on the relationships among the conductivity change, the integrated radiation dose and the content of chlorine introduced in the polyaniline film through radiation-induced doping.

Experimental

Samples. The polyaniline used in this experiment was chemically synthesized from a solution of aniline dissolved in 1 M perchloric acid. The resulting polyaniline was converted to the emeraldine base by repeated washing with a NaOH solution. The thus-prepared powder was dissolved in *N*-methyl-2-pyrrolidone; the solution was then poured onto a glass plate. The film was prepared by thoroughly evaporating the solvent at 80 °C under a vacuum for about 24 hours.

The polyaniline sample, as a prototype polyaniline dosimeter, consisted of a polyaniline strip (0.5 × 4 cm, *ca.* 40 μm thick) and PVC powder, which were sealed in a Pyrex glass tube (volume: *ca.* 2.5 cm^3) under vacuum or in air at 1 atm. In each glass tube, quartz wool was put between the strip and the powder so as not to contact them directly. The degree of polymerization of the PVC used was 1100, and its mesh size was about 150.

Irradiation. The samples containing a given amount of PVC were irradiated with γ-rays from ^{60}Co sources at room temperature. Irradiation above 100 Gy was carried out at the ^{60}Co irradiation facilities of Japan Atomic Energy Research Institute.

Measurement of Electrical Conductivity. The resistance of the polyaniline film was measured with an ultra-high resistance meter (Advantest Co., Model

R8340A) in a pure nitrogen atmoshere at room temperature. The original volume and surface conductivities of the undoped polyaniline film were measured with Au electrodes. After γ-ray irradiation, the glass ampoule of the sample was open, and the resistance of the irradiated strip was measured.

Neutron Activation Analysis of Chlorine. In order to examine the relationship between the conductivity change and the chlorine content of the strip, the content was determined by a method involving neutron activation analysis. After γ-ray irradiation, a piece of the strip was irradiated in a pneumatic tube of the JRR4 reactor in Japan Atomic Energy Research Institute. The intensity of the 2168-keV γ-ray of ^{38}Cl formed by the (n, γ) reaction of ^{37}Cl was measured with a Ge semiconductor detector system. The chlorine content was determined from its γ-ray intensity, compared with reference samples.

Results and Discussion

Conductivity Change of Irradiated Polyaniline. The volume conductivity of the undoped polyaniline film used in this experiment was 1×10^{-13} S/cm and the surface conductivity was 1×10^{-13} S. Figure 1 shows the change in the conductivity of the polyaniline film, itself, due to γ-ray irradiation. The abcissa represents the absorbed dose for thick polyaniline, and the ordinate shows the ratio of the conductivity of irradiated and non-irradiated polyaniline.

As Figure 1 shows, the film was found to be very resistant to radiation. Almost no conductivity change was observed up to 3.6 MGy in a film irradiated *in vacuo*. However, the conductivity of the film irradiated in air increased above *ca.* 0.1 M Gy, and reached 10^5 times the original conductivity at 3.6 MGy. This suggests that certain dopant gases are produced from the air, itself, in a high radiation field. Nitric acid is known to be formed in air due to radiation (*9, 10*). Nitric acid and/or NO_x gases are considered to be possible candidates to serve as dopants.

The polyaniline–PVC powder system. Figure 2 shows the conductivity change of irradiated polyaniline strips for polyaniline samples *in vacuo* with three different contents of PVC powder (10mg, 50mg, and 150mg). The conductivity increases almost linearly on a log–log plot along with an increase in the dose over a wide region of about 10 to 0.1 MGy; the maximun conductivity reached 10^{10} times its original value. This conductivity change is due to only a radiation-induced doping effect, because, as shown above, there was no conductivity change when the polyaniline was irradiated alone *in vacuo*. This linear relationship is one of the important characteristics required for an integrated radiation dosimeter. The conductivity showed a maximum at around 0.1 M Gy, and then decreased at

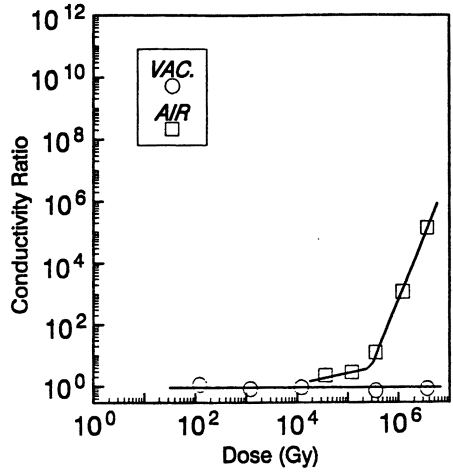

Fig. 1 Conductivity change of polyaniline film due to γ-ray irradiation

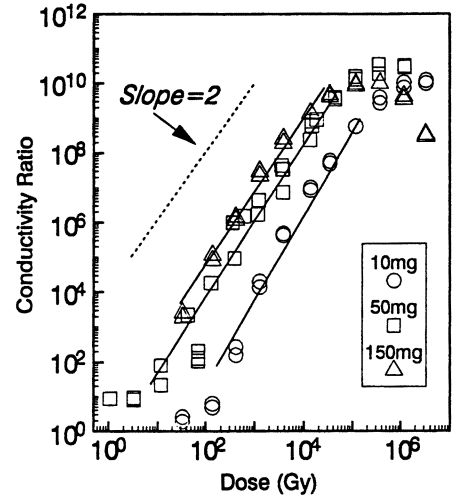

Fig. 2 Relationship between the dose and conductivity change of polyaniline film in the polyaniline–PVC system

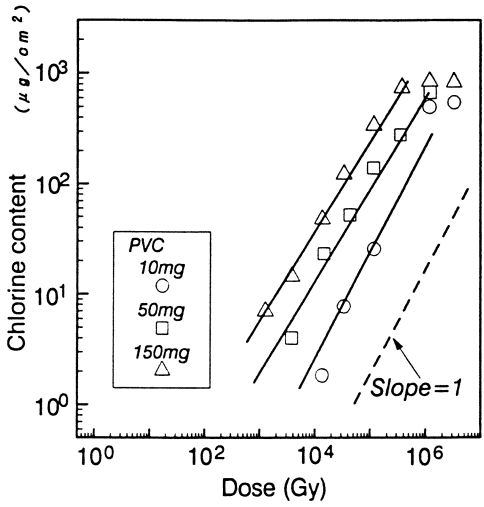

Fig. 3 Chlorine content on the surface of polyaniline film

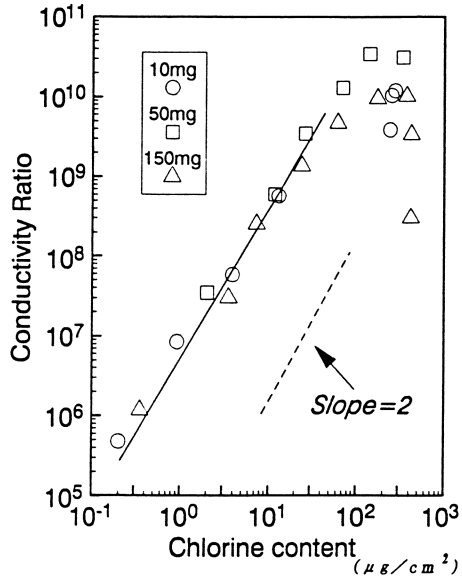

Fig. 4 Relationship between the chlorine content of polyaniline film and its conductivity change

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higher doses. The slopes of the fitting lines in the figure were about two, showing that the conductivity is proportional to the square of the dose.

On the other hand, the conductivity in polyaniline samples sealed with 50 mg of PVC powder in air increased by only a factor of 2 at 10^4 Gy. This result is considered to be due to a suppression of the diffusion of the heavy dopant gas by air.

The cross section of the doped polyaniline films was observed with a microscope. The micrographs indicated that the surface of the film was uniformly doped with dopants.

The gas produced from the γ-ray irradiated PVC powder was analyzed with a mass spectrometer. The dopant gas in this system was confirmed to be HCl, because only H_2 and HCl were detected in the mass spectra. Figure 3 shows the relationship between the content of chlorine in the irradiated polyaniline and the dose. The chlorine originally contained in undoped polyaniline was also determined to be *ca.* 10 μg per 1 cm^2 of the film based on a neutron activation analysis. The ordinate of Figure 3 represents the content in $\mu g/cm^2$, which was obtained by subtracting the original content from the content in the doped polyaniline. The content and dose exhibited a linear relationship with a slope of unity. This result indicates that the chlorine content is directly proportional to the dose. It was therefore found that the radiation-induced doping proceeded quantitatively along with an increase in the dose.

From Figures 2–3, the relationship between the chlorine content and the conductivity can be derived. There is a clear linear relationship with a slope equal to two, as shown in Figure 4. This exhibits that the conductivity is proportional to the square of the chlorine content. Figures 2–4 show that the decrease in the conductivity at a higher dose region than 0.1 MGy is not caused by a decrease in the chlorine content due to radiation effects. This decrease in the conductivity may be attributed to a saturation of the dopants on the surface and/or radiation effects on a surface which is highly doped with chlorine, in addition to a decrease in the production rate of the dopant gas due to the decomposition of PVC at a high-dose region.

The present results show that the polyaniline–PVC powder system is promising for wide-range integrated radiation dosimetry. A further study concerning the physico-chemical properties of the polyaniline film has been extensively carried out. The details will be reported elsewhere.

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