New polymer gel dosimeters consisting of less toxic monomers with radiation-crosslinked gel matrix

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Abstract. New polymer gel dosimeters consisting of less toxic methacrylate-type monomers such as 2-hydroxymethyl methacrylate (HEMA) and polyethylene glycol 400 dimethacrylate (9G) with hydroxypropyl cellulose (HPC) gel were prepared. The HPC gels were obtained by using a radiation-induced crosslinking technique to be applied in a matrix instead of a gelatin, which is conventionally used in earlier dosimeters, for the polymer gel dosimeters. The prepared polymer gel dosimeters showed cloudiness by exposing to 60Co γ-ray, in which the cloudiness increased with the dose up to 10 Gy. At the same dose, the increase in the cloudiness appeared with increasing concentration of 9G. As a result of the absorbance measurement, it was found that the dose response depended on the composition ratio between HEMA and 9G.

1. Introduction

Polymer gel dosimeters composed of monomers and a gel matrix are drawing attention as a tool of the three-dimensional dose distribution measurements in the radiation therapy [1]. The polymer gel dosimeters are based on the following chemical behaviours. The monomers in the gel matrix are polymerized by the irradiation, and then the polymers aggregate to induce cloudiness in the gel matrix. Accordingly, an absorbance of the gel increases with the dose. Three-dimensional dose distributions are imaged finally by Optical CT [2], X-ray CT [3], MRI [4] or ultrasound [5].

Many polymer gel dosimeters have been developed [6, 7]. Currently, either acrylamide or methacrylic acid as a monomer and gelatin as a matrix are used in promising polymer gel dosimeters [8-11]. Although the gelatin gel is preparable conveniently, there is a possibility of the disappearance of the three-dimensional dose distribution because of the re-melting of the gel at the temperature over 35ºC. On the other hand, since both acrylamide and methacrylic acid are harmful monomer, recipes for the polymer gel dosimeters consisting of less toxic monomers have been reported [12].

Polysaccharide derivatives such as carboxymethyl cellulose and carboxymethyl chitosan have been applied in industrial, medical, and agricultural fields because of safety and biodegradability. The polysaccharide derivatives usually undergo degradation by irradiation to a solid and a low-concentration aqueous solution. However, it was found that the gels of polysaccharide derivatives were obtained by γ-ray or electron beam irradiation to their highly concentrated aqueous solution without any crosslinker [13]. The gels prepared by a radiation-induced crosslinking technique show high water-absorption and thermal stability. Among the cellulose derivative gels, hydroxypropyl cellulose (HPC) gels are transparent materials [14].
In this work, we proposed new polymer gel dosimeters comprised of less toxic monomers and HPC gel prepared by radiation-induced crosslinking technique. Effects of the types of monomers and their composition ratios on the dose response of the polymer gel dosimeters were investigated.

2. Materials and methods

2.1. Preparation of HPC gels

HPC, which is the grade of 1000-5000 cP, was purchased from Wako Pure Chemical Industries, Ltd., Japan. Aqueous solution of 20 wt% HPC as a paste-state was sealed in polyethylene-nylon bags after pressing into a sheet of 1-mm thickness and degassing. The samples were irradiated to a dose of 10 to 70 kGy to obtain HPC gels. The irradiations were carried out using a Cockcroft-Walton type 2 MeV electron beam accelerator at the Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency. The obtained HPC gels were immersed into an excess amount of distilled water to remove uncrosslinked HPC, and then vacuum-dried. Gel fraction of the obtained HPC gels was determined gravimetrically by measuring insoluble part after water extraction of sol. Degree of swelling (Sw) of the gels was calculated from weight ratio, \((W_s - W_d) / W_d\), where \(W_s\) is the weight of the swollen gel and \(W_d\) is the weight of the dried gel.

2.2. Preparation of polymer gel dosimeters

The dried HPC gels were immersed into aqueous monomer solutions consisting of monomers (5 g), tetrakis(hydroxymethyl)phosphonium chloride (THPC) (0.16 g), and ultrapure water (94.84 g). The monomer solutions with various composition ratios were prepared by using 2 of 14 kinds of monomers such as methacrylate- and acrylamide-types. The swollen HPG gels were vacuum-packed to avoid exposure to air in the storage. The prepared samples were stored at 5ºC in a refrigerator until irradiation.

2.3. Irradiation

The prepared samples were irradiated up to 10 Gy by using a \(^{60}\text{Co}\) γ-ray source at the Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency. Dose rate was adjusted by varying the distance between the samples and source, which was in the range of 3.0 to 30 Gy/h. Dosimetry was preliminarily conducted with an ionization chamber. After irradiation, all samples were stored in the refrigerator.

2.4. Absorbance measurement

The absorbance of the polymer gel dosimeters were measured after 24 hours post-irradiation. The optical analysis was carried out using an ultraviolet and visible spectrophotometer (Hitachi High-Technologies Corporation, U-3310). The dose response of the polymer gel dosimeter was estimated from the absorbance at 660 nm as a function of dose.

3. Results and Discussion

Figure 1 shows the gel fraction and the degree of swelling (Sw) of HPC gels as the matrix of polymer gel dosimeters. The gel fraction of the HPC gel increased drastically up to 10 kGy to reach 75%, and then levelled off at about 90%. The Sw of the HPC gel swollen in pure water decreased from 26 to 8 at the dose of 10 to 70 kGy. Therefore, the HPC gel obtained at 10 kGy was selected as gel matrix for dosimeters because of the highest Sw. The Sw of the HPC gel swollen in each aqueous monomer solution exhibited in the range of 25 to 27. It was found that the Sw of the gel was independent of the type of monomers and their composition ratios. It would be worth noting that all of the swollen HPC gels were transparent.

Polymer gel dosimeters with 32 kinds of composition ratio were prepared by using 2 monomers which was selected from 14 monomers. Eighteen polymer gel dosimeters became cloudy by γ-irradiation at 10 Gy. It was found that 9 monomers can be utilized in the polymer gel dosimeter.
Among of them, methacrylate monomers such as 2-hydroxyethyl methacrylate (HEMA) and polyethylene glycol 400 dimethacrylate (9G) were efficient in terms of induction of the cloudiness of polymer gel dosimeter in comparison with acrylamide-type monomers such as acrylamide (AAm) and N,N'-methylene-bis-acrylamide (MBAAm). It is well known that polymer gel dosimeter comprised of AAm and MBAAm with gelatin, called PAG or PAGAT, became cloudy less than 10 Gy [15]. However, the polymer gel dosimeter with HPC gel matrix, which prepared by using the AAm/MBAAm aqueous solution, remained clear even at 10 Gy. This would be due to the effect of the matrix.

Figure 2 shows the photograph of the polymer gel dosimeters prepared by using the monomer solutions consisting of HEMA and 9G. The cloudiness of the polymer gel dosimeters increased with the dose. The polymer gel dosimeter comprised of HEMA and 9G at 3 and 2 wt%, respectively, exhibited higher cloudiness than that at 4 and 1 wt%. It was found that the polymer gel dosimeter with 3 wt% of HEMA and 2 wt% of 9G became cloudy at only 1 Gy. The absorbance measurement showed that the absorbance of the polymer gel dosimeters consisting of HEMA and 9G increased approximately linearly with an increase in the dose up to 10 Gy. The dose response that defined as the

![Figure 1: Gel fraction (a) and degree of swelling (b) of the HPC gels as a function of dose.](image)

![Figure 2: Photographs of the irradiated polymer gel dosimeters consisting of HEMA and 9G with HPC gel. The concentrations of HEMA and 9G are 4 wt% and 1 wt% (A), and 3 wt% and 2 wt% (B), respectively.](image)
initial increment of absorbance per unit dose depended on the concentration of the 9G. It was found, therefore, that the dose response can be adjusted by changing the composition ratio.

4. Conclusion
New polymer gel dosimeters were prepared by using the radiation-crosslinked HPC gel instead of a conventional gelatin gel. The polymer gel dosimeters comprised of less toxic methacrylate-type monomers such as HEMA and 9G and HPC gel showed the cloudiness at only 1 Gy of 60Co $\gamma$-irradiation. The absorbance of the polymer gel dosimeter at 660 nm increased approximately linearly with the dose up to 10 Gy. The dose response depended on the composition ratio between HEMA and 9G. It is expected that development of more sensitive polymer gel dosimeters can be achieved by selecting the kinds of monomers and optimizing their composition ratios.

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6. References
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