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Rate of elapsed polymerization of hydroxyethylacrylate gel induced by gamma irradiation

Khalid Ahmed RABAEH[1,*] Elias SAION[1] Mohammad Ahmed Ali OMER[1]
Azhar Abdul RAHMAN[1] Mohammad Yusif HUSSAIN[1] Shahrim ISKANDAR [1]
Noria Mohammad ALI[2]

[1] *Department of Physics, Universiti Putra Malaysia 43400 UPM Serdang, Selangor, Malaysia*

[2] *Nuclear Agency of Malaysia, 43000 Kajang, Selangor, Malaysia*

Abstract The rate of elapsed polymerization of polyhydroxyethylacrylate in gelatin has been studied to investigate the effect of co-monomers consumption at a given dose. The polymer gel dosimeters consisted of 2%~4% *N*,*N*-methyelene-bis-acrylamide cross-linker, 2%~4% 2-hydroxyethylacrylate monomer and gelatin at 3% and 5%. The dosimeters were irradiated by using ^{60}Co teletherapy γ-ray source up to 20 Gy at a constant dose rate. The relaxation rate of water proton in the dosimeters at different doses and co-monomer concentrations were measured using a nuclear magnetic resonance spectroscopy. The rate of elapsed polymerization decreases with increasing the dose and the initial concentration of co-monomers. The rate of consumption of co-monomers increases with an increase of the polymerization and the gelatin content of the polymer gel.

Key words Elapsed polymerization, Relaxation rate, Consumption rate, Polymer gel dosimeter

CLC number O631.3$^+$4

1 Introduction

Recent development of complex radiotherapy treatment techniques has emphasized the need for a dosimetric system with the ability to measure absorbed dose distributions in 3D and with high spatial resolution[1]. The Fricke or ferrous sulphate dosimeter in gelatin could be used by investigating changes in nuclear magnetic resonance (NMR) longitudinal (T_1) and transverse (T_2) relaxation times with dose due to the radiation-induced conversion of Fe^{2+} ions to Fe^{3+} ions[2]. A major limitation in ferrous sulphate gel systems is the diffusion of Fe^{3+} ions within the dosimeter after irradiation, resulting in the change of dose distribution with time[3]. Since reported by Maryanski *et al*[4], polymer gel dosimeters have been used to solve this problem[5,6]. The original polymer gel is based on the high molecular weight compounds consisting of a monomer, acrylamide (AAm) and a cross-linker, *N, N*' methyelene-bis-acrylamide (BIS)[7] dissolved in a gelatin or agarose hydrogel. Upon irradiation, water molecules are dissociated into OH and H radicals that can attack the double C=C bonds of co-monomers (AAm and BIS). The formed co-monomer radicals, in turn, interact with other co-monomers and produce a chain reaction to form 3D polymer aggregates that are spatially retained in a gelatin matrix. The amount of polymer formed is related to absorbed dose involved in the polymer gel dosimeter system. These polymer aggregates are usually evaluated using NMR or Raman spectroscopy techniques. However, the dose response of polymer gel dosimeters increases with increase of initial concentration of co-monomers and decrease of the gelatin concentration[8,9]. In this article, we report the rate of elapsed polymerization of polymer gel dosimeter in

* Corresponding author. *E-mail address:* elias@putra.upm.edu.my
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order to demonstrate the effect of consumption of co-monomers on radiation-induced polymerization.

2 Materials and methods

2.1 Synthesis of polyhydroxyethylacrylate (PHEA) gel dosimeters

The PHEA polymer gels were composed of 2-hydroxyethylacrylate (HEA) monomer, *N*,*N'*-methylene- bis-acrylamide (BIS) cross-linker, gelatin (Type A, 300 bloom), and de-ionized water at appropriate weight fraction respectively. All co-monomers (HEA and BIS) were obtained from SIGMA Chemical Co., USA. The total concentration of co-monomers (%T, by weight) is given in Table 1. The polymer gels were synthesized in a nitrogen glove-box according to Gustavsson *et al*[10]. After deoxygenating the de-ionized water for a minimum of 2 h, the gelatin was added and magnetically stirred. The gel solution was heated up at 45℃ for 1 h, before adding HEA and BIS co-monomers. The polymer gels were kept stirring at 45℃ until the co-monomers were completely dissolved. Throughout, the polymer gels were purged with nitrogen at least 5 h continuously during the mixing in order to expel oxygen that inhibits polymerization prior to gamma irradiation[7].

Table 1 Composition (in wt%) of PHEA polymer gels

Water	Gelatin	HEA	BIS	%T
91	5	2	2	4
89	5	3	3	6
87	5	4	4	8
93	3	2	2	4
91	3	3	3	6
89	3	4	4	8

The aqueous solution added with gelatine at first and then solved with HEA and BIS co-monomer was kept stirring at 45℃ for 5 h prior to gamma irradiation in a nitrogen glove-box according to Gustavsson *et al*[10]. The final gel solution was filled into sealed 5 mm ampuole tubes or P6 class vials. All polymer gel solution was stored in a refrigerator at 10℃ overnight to solidify for gamma irradiation in the following day.

2.2 Irradiation

The irradiation was carried out in a ^{60}Co source (Eldorado 8, for teletherapy, Atomic Energy of Canada Limited) with the maximum dose rate of 0.43 Gy/min calibrated using a Fricke dosimeter. Each dosimeter vial filled with PHEA was placed in a polystyrene holder in a water-phantom acrylic tank. The sample was irradiated with absorbed dose ranging from 0 to 20 Gy at 15 cm depth, 60 cm (SSD) set-up and 10cm×10 cm field size. The sample was transferred back to the refrigerator and kept for about 3 days before NMR measurement.

2.3 NMR measurements

A Carr Purcell Meiboom Gill (CPMG) sequence or spin-echo pulse method (90^o–τ–180^o) was used to measure the relaxation rate. The relaxation rates were measured using an NMR instrument analysis from Bruker at frequency of 20 MHz and the magnetic strength of 0.47 T. This spectrometer was specifically designed for proton relaxation measurement. All polymer gel dosimeters were transferred to the temperature controlled NMR room to equilibrate the gels to room temperature prior to NMR measurement.

3 Results and discussion

3.1 Rate of polymerization, R_2

The relaxation rate, R_2, which corresponds to the amount of polymer formation in PHEA gel and increases with absorbed dose in 0~20 Gy, can be described by Eq.(1)[11]:

$$R_2 = R_0 + A(1 - e^{-D/D_0}) \quad (1)$$

where R_0 is the relaxation rate at zero dose, D is the dose, D_0 is the dose sensitivity parameter, and A is a constant. As the dose increases, more free radicals were generated and induced the breakage of C=C bonds of the co-monomers (HEA and BIS), resulting in the formation of more free radicals fragments to produce PHEA. A linear dose response can be seen at low dose region from 2 to 6 Gy. At higher doses (6 to 20 Gy), the dose response changes dramatically towards the saturation. The polymerization is terminated when one of the co-monomers has been

completely consumed. The best mono-exponential fit of changes in the proton relaxation rate $\Delta R_2=R_2-R_0$ versus absorbed dose for polymerization of PHEA gel for different %T from 4% to 8% and at a given gelatin concentration is shown in Fig.1.

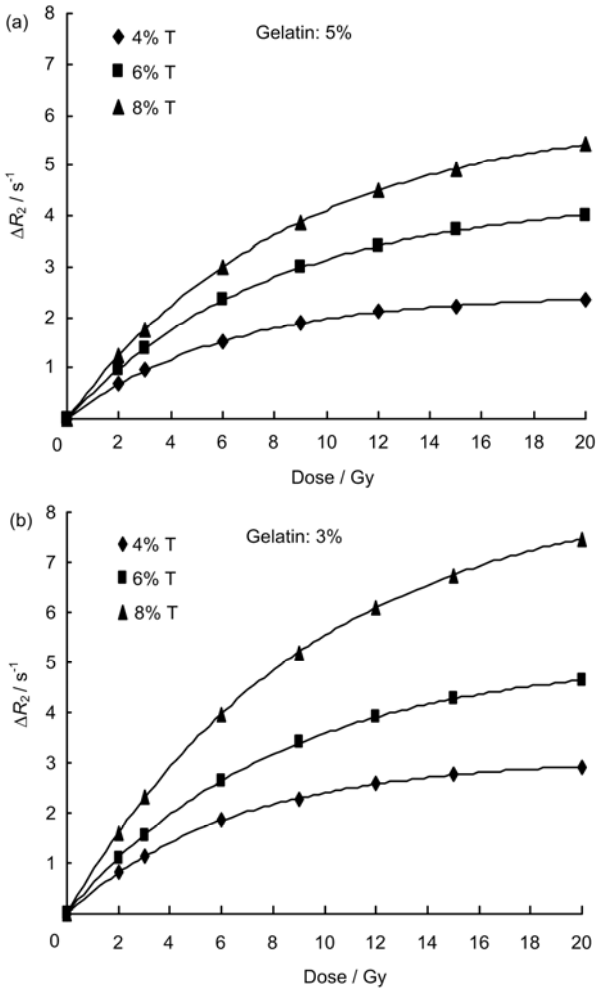

Fig.1 Change in transverse relaxation rate (ΔR_2) of PHEA gel versus dose at 5% gelatin (a) and 3% gelatin (b) for different concentrations of co-monomers.

To make a decision of a linear dose response with three points is not correct according to the correlation coefficient from three points. The polymerization cannot be terminated when monomer HEA or cross-linker BIS is completely consumed. And the cross-linking should not be continued when closs-linker BIS is consumed. It means that the polymerization should occur if the HEA still exists though BIS is consumed.

The correlation between the relaxation rate (ΔR_2) of PHEA gel versus dose cannot make the dosimeter to be used.

Eq.(1) can be rearranged according to Eq.(2).

$$\left(1-\frac{\Delta R_2}{A}\right)=\mathrm{e}^{-D/D_0} \tag{2}$$

D_0 can then be determined from the slope of the linear plot of $\ln(1-\Delta y/A)$ versus dose D. The results show that D_0 value increases gradually with increasing %T (Fig.2). The dose correlation factor (η) of PHEA polymer gels can be taken from the slope of D_0 versus %T. The η values increase from 0.65 to 0.95 Gy per %T for 3% gelatin and from 0.61 to 0.86 Gy per %T for 5% gelatin, which indicate that the polymerization decreases considerably with increasing concentration of gelatin. The same result has been reported previously for PHEA gel dosimeter[10] measured by using FT Raman spectroscopy.

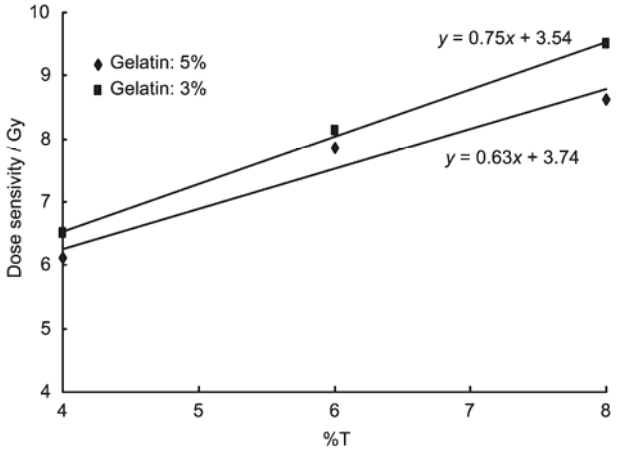

Fig.2 Correlation between dose sensitivity D_0 values and the initial total concentration of co-monomers (%T) for different concentrations of gelatin.

3.2 Rate of elapsed polymerization, dR_2/dt

The absorbed dose (D) at a certain point inside the irradiated material after a period of irradiated time (t) is given by Eq.(3):

$$D(t)=k\,t \tag{3}$$

where k is the dose rate, which varies with different sources and different distances (SSD) from source to sample surface. Eq.(1) can be written as

$$R_2=R_0+A(1-\mathrm{e}^{-k\,t/D_0}) \tag{4}$$

The change in relaxation rate or radiation response at time dt can be obtained by differentiation of Eq.(4).

$$\frac{\mathrm{d}R_2}{\mathrm{d}t}=\frac{Ak}{D_0}\mathrm{e}^{-D/D_0} \tag{5}$$

The physical meaning of the exponential Eq.(5) is the rate of elapsed polymerization of PHEA polymer gels, which indicates the degree of polymerization after a particular dose has elapsed due to consumption of co-monomers. However, in this work, the new term can be derived from NMR spectroscopy measurements. Ak/D_0 is the initial rate of elapsed polymerization representing the maximum value of the rate of elapsed polymerization. Fig.3 shows the rate of elapsed polymerization for PHEA polymer gels as a function of dose at %T from 4% to 8% and for a given gelatin concentration. For all concentrations of HEA and BIS the rate of elapsed polymerization of PHEA polymer gels decreases with increasing dose, which can be seen from the exponential decay of the individual dR_2/dt *vs.* dose curve.

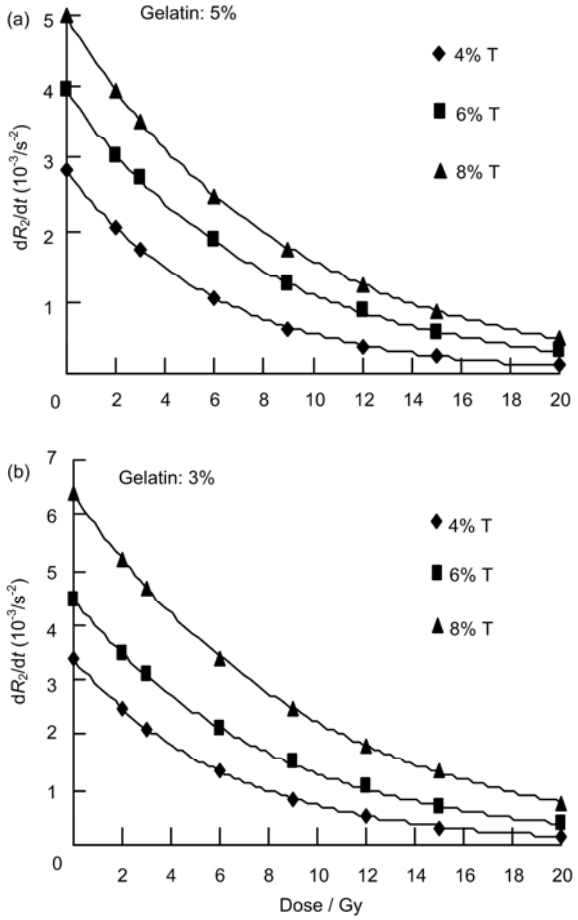

Fig.3 Rate of elapsed polymerization of PHEA gel *vs.* dose at 5% gelatin (a) and 3% gelatin (b) for different co-monomer concentrations.

At 4% T the rate of elapsed polymerization decreases with absorbed dose following Eq.(5). At low doses the rate of elapsed polymerization shows significant difference for %T from 4% to 8%. The 8% T shows higher value because the initial rate Ak/D_0 of elapsed polymerization is higher. At higher doses the rate of elapsed polymerization decreases dramatically due to the consumption of co-monomers. In this case the rate of elapsed polymerization is immediately ceased when one of the co-monomers is completely consumed. The rate of elapsed polymerization increases by decreasing the gelatin concentration of PHEA from 5% to 3% (Fig.3) because less free radicals are consumed by gelatin molecules. Thus, lower gelatin concentration leads to an increase in number of radicals available for initiation of the polymerization process[10], resulting in a greater rate of elapsed polymerization.

3.3 $D_{1/2}$ of rate of elapsed polymerization

The half dose $D_{1/2}$ is commonly used to interpret exponentially decaying radiation events such as reduction of radiation intensity along the path or decay of nuclear radioactivity over time. The half dose represents the amount of dose required to produce 50% of the maximum value of radiation event or in our case is the initial rate of elapsed polymerization of PHEA polymer gels, which can be easily derived from Eq.(5) to be $D_{1/2}=D_0\ln 2$. Fig.4 shows the value of $D_{1/2}$ increases gradually with increasing total co-monomer concentration (%T) from 4% to 8%. The increase of $D_{1/2}$ leads to the increase of the rate of elapsed polymerization of PHEA polymer gels.

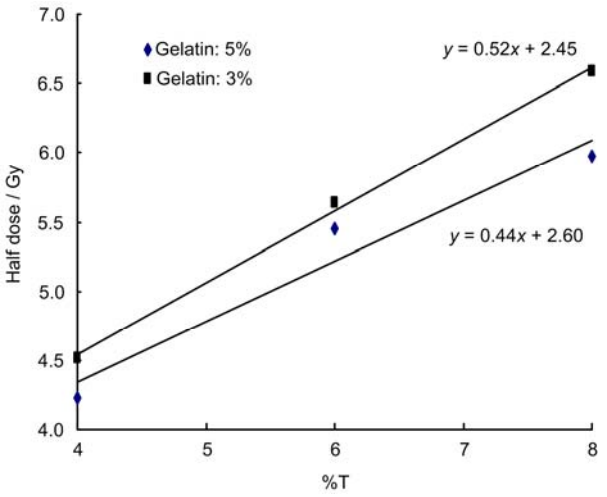

Fig.4 Correlation between initial rate of elapsed polymerization value and the initial total concentration of co-monomer (%T) for different concentrations of gelatin.

The $D_{1/2}$ values are higher for lower gelatin concentrations. The results also show that there is a linear correlation between $D_{1/2}$ values and (%T) concentrations from 4% to 8%. The correlation dose factor ζ of the rate of elapsed polymerization in PHEA polymer gels can be taken from the slope of $D_{1/2}$ versus %T at a given gelatin concentration. The ζ values increase from 0.44 to 0.52 Gy per %T for gelatin concentrations from 5% to 3%, indicating the rate of elapsed polymerization increases with decreasing the concentration of gelatin.

4 Conclusions

Radiation-induced rate of elapsed polymerization PHEA polymer gel dosimeters in absorbed doses of up to 20 Gy have been studied using NMR spectroscopy. The relaxation rate (R_2) increases with absorbed dose and follows a mono-exponential equation. The rate of elapsed polymerization decreases with absorbed dose and follows an exponential equation. The half dose ($D_{1/2}$) increases with the total concentration of co-monomer (%T), providing better understanding of the effects of co-monomer concentrations in the polymerization process. The dose correlation between $D_{1/2}$ and %T for PHEA polymer gel at 3% gelatin is always greater than that of PHEA polymer gel at 5% gelatin, which indicates that HEA reacts with BIS more efficiently at lower concentration of gelatin.

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