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Dose Correlation Factor of Polymer Formation and Copolymer Consumptions of Polyacrylamide Gels

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Abstract: The half dose sensitivity parameter $D_{1/2}$ for polymer formation and co-monomer consumptions of polyacrylamide gel dosimeters used in 3D verification of radiotherapy treatment planning has been studied using Raman spectroscopy. The polymer gels consist of acrylamide as monomer and N, N' methyelene-bis-acrylamide as crosslinker at various compositions from 2 to 6%, 6% gelatine and completed with deionised water. The dosimeters were irradiated up to 20 Gy with ^{60}Co gamma rays at a constant dose rate to form polyacrylamide gels. The polymerisation was followed from the increase in Raman intensity with increasing dose at 3040 cm^{-1} for CH_2 symmetric stretching mode assigned to polyacrylamide. The consumptions of the co-monomers were followed from the decrease in Raman intensities at 1663 and 1628 cm^{-1} for C=C stretching modes assigned to acrylamide and bis-acrylamide, respectively. The correlation between $D_{1/2}$ and concentrations of monomer and crosslinker produce the dose correlation factor k_M and k_B for acrylamide and bis-acrylamide, respectively. The dose correlation factor k_B is greater than k_M, indicating the crosslinker reacts more efficiently than the monomer to produce 50% of the polyacrylamide.

Key words: Polymer gel, polyacrylamide, Raman spectroscopy, dose correlation factor

INTRODUCTION

Polymer gel dosimeter used in conjunction with magnetic resonance imaging (MRI) is the most popular dosimeter imaging modality as a potential use for 3D conformal mapping of complex dose distribution[1-4]. Many researches are focused to manufacture more efficient and excellent stability 3D dosimeters that have the highest dose resolution so that two doses of slightly different values can be mapped and visualised correctly with the lowest uncertainty[1,5]. The emphasis in the current literatures has been on the dose resolution optimisation of polymer gel dosimeters using different monomers[6-10].

Recently, there has been more attention on the study of the basic physical and chemical properties of polymer gel dosimetry, which could provide invaluable information on the various factors affecting the overall performance of a polymer gel dosimeter[11-15]. The sensitivity of polymer gels is dependent on physical parameters such as radiation energy, temperature during MRI evaluation time between irradiation and NMR evaluation and magnetic strength has been reported[12]. Murphy *et al.*[2] have observed the effect of pH during synthesis on the dose response of a modifier polymer gel dosimeter. It is well known fact that dose response of gel dosimeters is dependent on the temperature during MRI measurement[7,16].

There has been shown that the dose response of polymer gel dosimeters increases linearly with the initial concentrations of co-monomers and the gelatine concentration using FT-Raman spectroscopy[17]. Polymer formation and co-monomer consumption have been observed in the Raman spectra[11,14]. Their information can be determined from the dose sensitivity parameter D_0 or the half dose $D_{1/2}$ = In $2D_0$. From these studies it was found that the crosslinker is consumed at a greater rate than the monomer in polyacrylamide gels. The rate of polymer formation is equal to that of the monomer. Nevertheless, these studies are by no means complete and more work is needed to understand the behaviour of initial concentrations of monomer and crosslinker on the dose correlation factor of polymerisation. This study was concerned with the dose resolution correlation factor of polymerization and consumption of monomer/crosslinker to produce 50% of the polymer formation in polyacrylamide gel dosimeters.

MATERIALS AND METHODS

Synthesis of polymer gel: The polyacrylamide gel dosimeters were synthesised in a nitrogen glove-box to

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avoid from oxygen-induced polymerisation before irradiation. Both compositions of acrylamide and bis-acrylamide were varied from 2 to 6% and completed with 6% gelatine and deionised water. Both co-monomers were obtained from SIGMA chemical Co (St. Louis, Mo, USA) and were of electrophoresis grade (99%). The co-monomer and gelatine were dissolved separately in two reaction flasks with equal amounts of the total water volume. In the first reaction flask, the monomer and crosslinker in half of the amount of deionised water were heated to a constant temperature of 55°C for 2 h. In the second reaction flask, the gelatine and the other half of the amount of deionised water were also heated to a constant temperature of 55°C for 2 h to dissolve the gelatine.

Subsequently, both solutions were allowed to cool down to 30°C for about 1 h to avoid spontaneous heat-induced polymerisation before mixing. A peristaltic pump was used to mix the monomer with the gelatine via Tygothane flexible tubing and stirred at 1000 rpm to form polyacrylamide gel. The gel was pumped into screw-top P6 glass vials using another peristaltic pump. The manufacture and collection of the gel dosimeters were conducted in oxygen free environment of a glove box, which was flushed with nitrogen to expel oxygen that inhibits polymerisation prior to gamma irradiation. The oxygen concentration was maintained at less than 0.1 mg L^{-1}. The final gel dosimeters were sealed and keep in a refrigerator before irradiation.

Irradiation and copolymerization reactions: The irradiation was carried out using the gamma source, Eldorado 6 and 8 Co-60 teletherapy (Atomic Energy of Canada Limited) with a dose rate at 0.58 Gy min^{-1}, which had been calibrated. Each PAG vial was placed in a polystyrene holder in an acrylic water phantom tank. The samples were irradiated with gamma rays with dose ranging from 1 to 30 Gy at 15 cm depth, 60 cm Surface to Source Distance (SSD) set-up, 60x60 cm^2 field size. The phantom temperature during irradiation was constant at 25°C.

Radiation induced polymerisation in polymer gel dosimeters has been discussed by many authors[15,17]. On exposure of the polyacrylamide to ionising radiation a number of reactions are initiated including the initial formation of ionisation and excitation of molecules and free radical species. The reaction between radical fragments and co-monomer ultimately lead to the formation of an insoluble polymer gel network in the gelatine matrix. After the initial formation of ionised and free radical species (H^*, OH^* or R^*) (Eq. 1), initiation of the polymerisation process occurs via addition of free-radical fragments to the co-monomers (M) presence in the solution (Eq. 2). Thus propagation results in the formation of high molecular weight copolymers (Eq. 3). Proportions of growing macro radicals will become less accessible and possibly undergo slow reaction with co-monomer species and eventually terminated (Eq. 4).

$$H_2O + \gamma \rightarrow H^* + OH^* \quad \text{(Radiolysis)} \qquad (1)$$

$$RH + OH^* \rightarrow R^* + H_2O \qquad (1a)$$

$$RH + H^* \rightarrow R^* + H_2 \qquad (1b)$$

$$R^* + M \rightarrow \overset{*}{RM} \quad \text{(Initiation step)} \qquad (2)$$

$$\overset{*}{RM} + M \rightarrow \overset{*}{RM} \quad \text{(Propagation)} \qquad (3)$$

$$\overset{*}{RM} + M_1 \rightarrow MAA \rightarrow \overset{*}{RM} \qquad (3a)$$

$$\overset{*}{RM} + M_2 \rightarrow BIS \rightarrow \overset{*}{RM} \qquad (3b)$$

$$\overset{*}{RM} + \overset{*}{RM} \rightarrow \text{dead polymer} \quad \text{(Termination)} \qquad (4)$$

The reaction between radical fragments and acrylamide monomer ultimately lead to the formation of an insoluble polyacrylamide network in the gelatine matrix. Figure 1 shows the chemical structure of acrylamide, crosslinker bis-acrylamide and polyacrylamide.

Raman spectroscopy: Raman spectra were measured using Raman spectrometer (RSI 2001 B, Raman system, INC) equipped with 532 nm solid-state diode green laser. Grams/32, version 6 software was used to analyse the spectra. All spectra were corrected for base line; smoothing and Fourier Transform (FT). The baseline correction utilised the multiple point level method in which the baseline is levelled at a value that is the average of the baseline points. A constant correction factor of 80% of the degree of smoothing parameter was used throughout the data collection. The Fourier smoothing was accomplished by the peak data, applying a triangular filter function at the specified cut-off point of 40% and then reverse Fourier transforming the data.

The vibrational Raman effect is especially useful in studying the structure of polyatomic molecules such as polymers. When a transparent medium is irradiated with a high power monochromatic photon beam such as laser, the electric field of incident photons may induce an electric dipole in the molecules. Most of the photons will be scattered coherently (Rayleigh scattering) with no lost in energy and some will undergo inelastic scattering (Raman scattering). The inelastic photons emerge with the shift of wavelength $v' = v \pm \Delta v$; where, v is the frequency

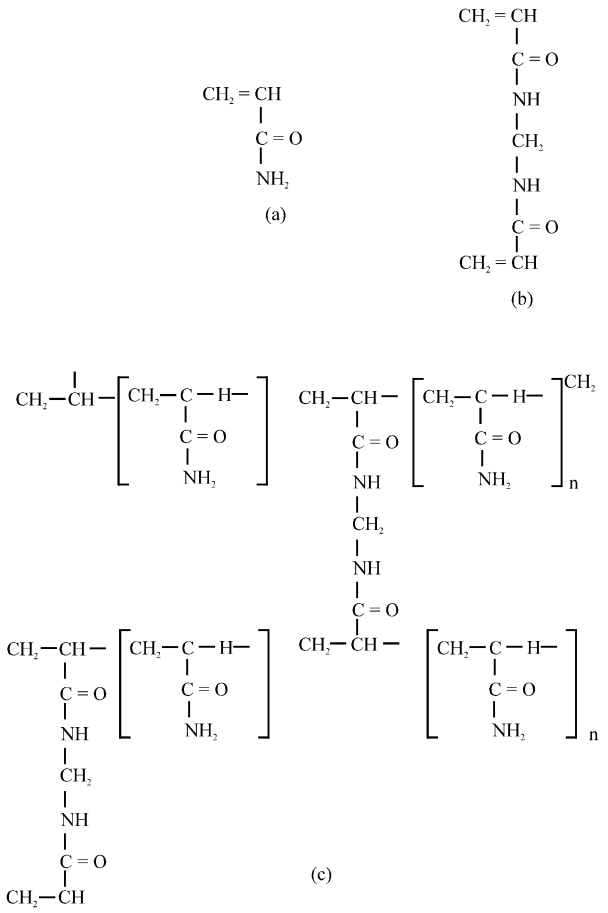

Fig. 1: Chemical structure of (a) Monomer Acrylamide (AA), (b) Crosslinker bis-acrylamide (BIS) and (c) Polyacrylamide (PAA)

of incident photons and Δv corresponds to the energy level of the various molecular vibrations due to stretching and bending motions of atoms. The energy of the scattered radiation is less than the incident radiation, for the Stoke line or hv' = hv-hΔv and for the anti-Stoke line the energy is more than the incident energy, or hv' = hv+hΔv; where, h is the Plank's constant. Experimentally, only the Stokes shift is observed in Raman spectra, since Rayleigh and anti-Stoke are filtered out by measuring instrument. A Raman spectrum represents the intensity of the scattered radiation as a function of energy difference between incident and scattered photons. Thus, the peak in Raman spectrum represents the vibrational energy hΔv of a particular covalent bond of molecular species. Experimentally the intensity of the Raman (Stoke) scattering can be expressed as $I = k'CI_0v^4 \exp(-h\Delta v/kT)$; where, k' is a constant of the instrument, C is the concentration of the species responsible for the scattering, I_0 is the intensity of the incident beam, k is the Boltzmann constant, T is the absolute temperature. Given constant conditions of typical Raman experiment, the intensity is therefore proportional to the concentration of the species only.

RESULTS AND DISCUSSION

Formation of polyacrylamide: The polymerization was followed from the increase of the intensity of Raman peak with increasing dose at 3040 cm^{-1} for CH_2 symmetric stretching mode assigned to polyacrylamide. The relationship between Raman intensity and dose reveals positive monoexponential behaviour for polymer formation in the dose range between 0 and 20 Gy. The

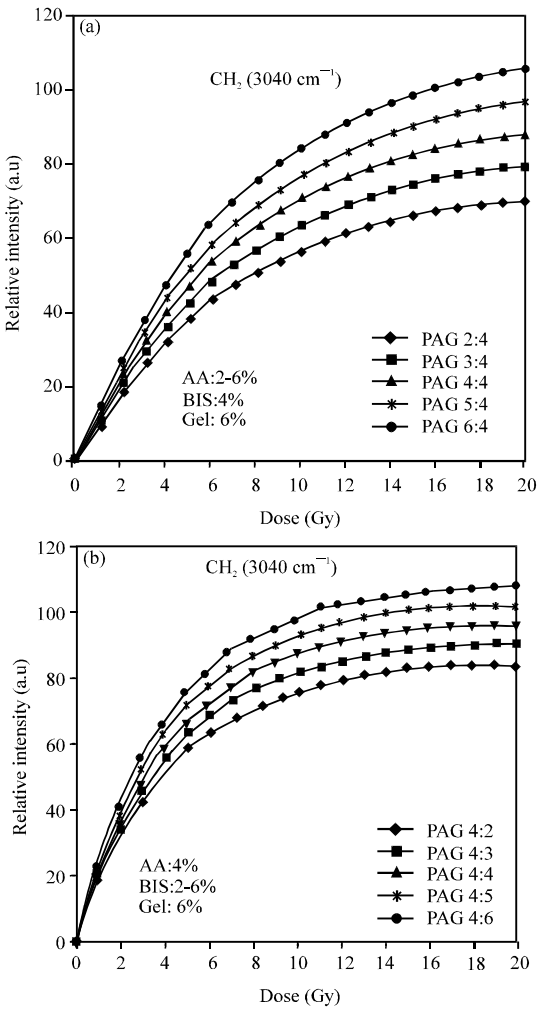

Fig. 2: Monoexponential function of Raman intensity Δ*y* vs. dose D for polymerization process of polyacrylamide gel (PAG) for (a) 4% BIS at various AA from 2 to 6% and for (b) 4% AA at various BIS from 2 to 6%

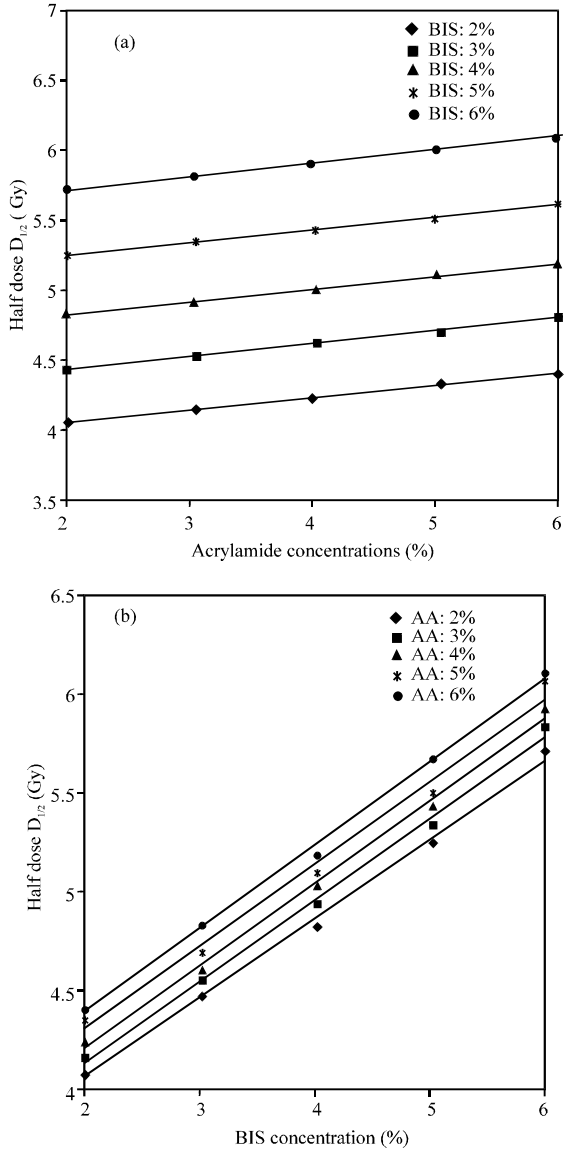

Fig. 3: The polymerization process shows the correlation between (a) $D_{1/2}$ vs. % AA at various BIS from 2 to 6% and (b) $D_{1/2}$ vs.% BIS at various AA from 2 to 6%

intensity, y, as a function of dose D can be fitted to the functional form[14]:

$$y = y_0 + A(1 - e^{-D/D_0}) \quad (5)$$

Where, D_0 is the sensitivity parameter, y_0 is the Raman intensity at zero dose and $A = y_{max}-y_0$ is the maximum differential dose response. y_{max} is the maximum intensity over the dose range up to 20 Gy. Figure 2a and b illustrate the positive exponential plots of the intensity change $\Delta y = y-y_0$ as a function of absorbed dose D at initial concentrations of acrylamide and bis-acrylamide, respectively. The dose sensitivity parameter D_0 was determined from the reciprocal of the slope of a linear plot $\ln\left(1-\frac{\Delta y}{A}\right)$ versus D. The linear correlations between $D_{1/2}$ and the initial concentrations of AAM and BIS produce the gradients k_M and k_B, which are illustrated in Figure 3 a and b, respectively. The parameters k_M and k_B are defined as the dose resolution of acrylamide and bis-acrylamide to produce 50% of the polymer formation. Note that $k_B > k_M$, which indicates that bis-acrylamide reacts more efficiently than acrylamide to produce 50% of the polyacrylamide.

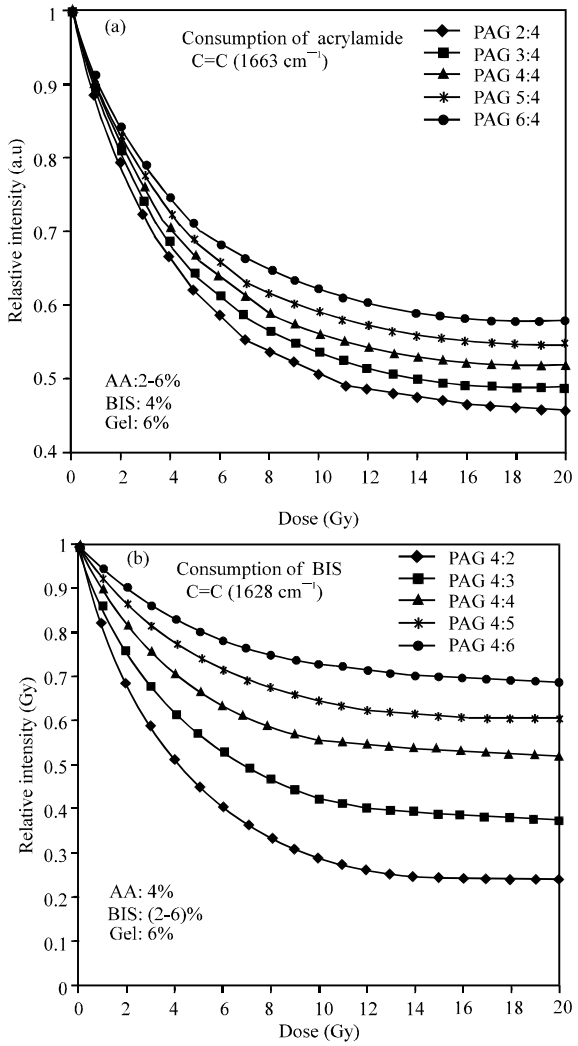

Fig. 4: Monoexponential function of Raman intensity ΔY vs. dose D (a) 4% BIS at various AA from 2 to 6% for consumption of AA and (b) 4% AA at various BIS from 2 to 6% for consumption of BIS

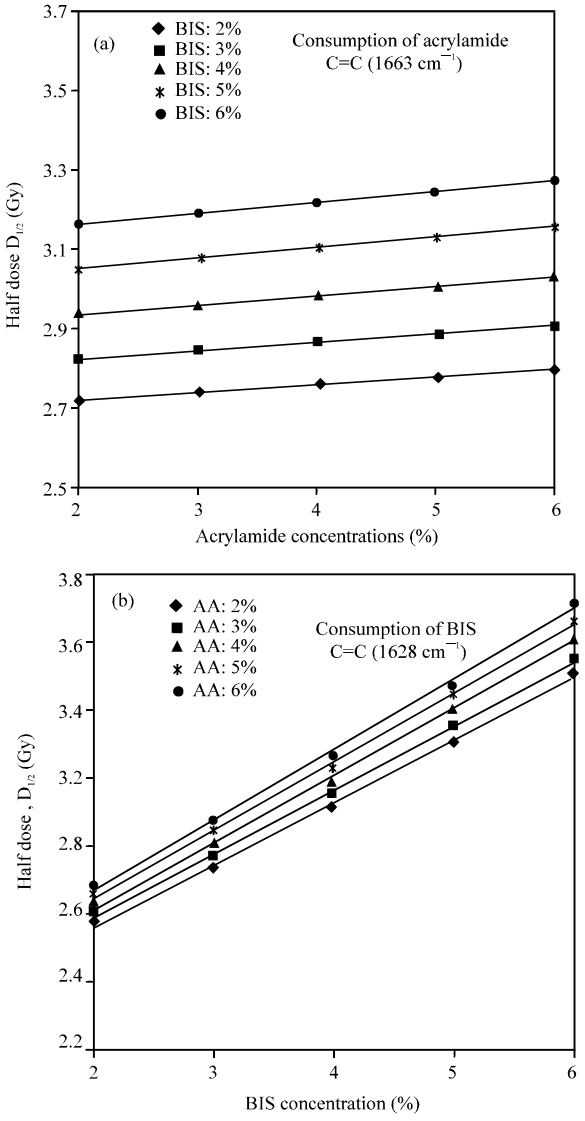

Fig. 5: The co-monomer consumption process show the correlation between (a) $D_{1/2}$ vs. % AA at various BIS from 2 to 6% and (b) $D_{1/2}$ vs. % BIS at various AA from 2 to 6%

Consumption of acrylamide and bis-acrylamide: The consumption of acrylamide and bis-acrylamide was followed from the reduction of Raman intensities at 1663 and 1628 cm^{-1} assigned to C = C stretching mode of acrylamide and bis-acrylamide, respectively. Both Raman intensities for acrylamide and bis were fit to the functional form:

$$y = y_0 - A(1 - e^{-D/D_0}) \quad (6)$$

Figure 4 a and b show the negative monoexponential plots of the intensity change $\Delta y = y - y_0$ as a function of absorbed dose D at initial concentrations of acrylamide and bis, respectively. The linear correlations between $D_{1/2}$ and the initial concentrations of Aam and BIS produce the gradients k_M and k_B, which are shown in Fig. 5 a and b, respectively. The parameters k_M and k_B are defined as the the dose resolution of acrylamide and bis to produce 50% of the co-monomer consumptions. Note that $k_B > k_M$, which indicates that bis consumes more efficiently than acrylamide to produce 50% of the polyacrylamide.

CONCLUSIONS

This study has presented the effects of initial concentration of acrylamide and bis-acrylamide on radiation-induced polymerisation of polyacrylamide gel dosimeters. The dose response relates to the increase of polymerisation of polyacrylamide with increasing dose. The change in Raman intensity is monoexponential of the form $\Delta y = (A1 - e^{-D/D0})$ in dose range up to 20 Gy. The half dose sensitivity $D_{1/2}$ increases with the concentration of acrylamide and bis-acrylamide, which provide better understanding of the effects of co-monomer concentrations in the polymerization of polyacrylamide and the consumption of monomer and crosslinker. The dose correlation factor of crosslinker k_B is always greater than the dose resolution k_M, which indicates crosslinker reacts more efficiently than monomer to produce 50% of the polyacrylamide and the consumptions of co-monomers. Bis-acrylamide is consumed more efficiently than acrylamide in the formation of polyacrylamide. The consumption of bis-acrylamide is constant irrespective of monomer concentrations.

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