

Synthesis and Characterization of Poly(Acrylamide-Co-Methacrylamide) Gels Material using Raman Spectroscopy

Aris Doyan^{1,a} and Susilawati^{1,b}

¹Departement of Physics Education, Faculty of Mathematic and Sciences Education, University of Mataram, Lombok NTB Indonesia

^aarisdoyan@yahoo.co.id, ^bsusilawatihambali@yahoo.co.id

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Abstract. In Raman spectroscopy, the inelastic scattering intensity of light is detected after the incident light interacts with the sample. The difference in energy between incident and scattered light is absorbed by the sample in the form of molecular vibrations. Each molecule in the sample has a characteristic set of vibrational modes due to covalent bonds. Fourier Transform Raman spectroscopy was used to investigate the effect of ionizing radiation on polymerization of polymer gels for radiation dosimetry. In the formation of polyacrylamide-co-methacrylamide, Raman intensity was taken at 3040 due to CH₂ stretching modes for the consumption of both monomers. It has been found that the relationship between Raman intensity and dose is monoexponential in which the dose response curves of the formation of polymer and the consumption of monomers and BIS of Raman intensity y at given dose D can be described in the form $y = y_0 + A[1 - \exp(-D/D_0)]$, where y_0 is the Raman intensity at zero doses, A is a constant and D_0 is the dose sensitivity. In this work the dose sensitivity of polymerization may be represented by the change in Raman intensity Δy as a function of dose D for different concentrations of monomer (%M) and cross-linker (%C) by weight. In this case, $\Delta y = y - y_0$ where y is the Raman intensity at dose D . The dose sensitivity D_0 is then determined by fitting the response curves. For PAAm-co-MAAmG system at constant cross-linker, the concentration of MAAm monomer is greatly influenced the dose sensitivity of polymerization. D_0 obtained from PAAm-co-MAAmG system is always greater than that of the PMAAmG and PAAmG systems, which implies that PAAm-co-MAAmG system at 2% BIS cross-linker is less radiosensitive than those of PMAAmG and PAAmG systems. The parameter k_B of MAAm is always greater than that the parameter k_A of AAm, indicating the dose resolution of polymerization of PAAm-co-MAAmG system is controlled by the MAAm monomer rather than the AAm monomer.

Introduction

One of the first applications of Raman spectroscopy to polymer gels used in radiotherapy who able to qualitatively characterize the consumption of acrylamide (AAm) and BIS as a function of dose. They described that the Raman technique is more direct than MRI dosimetry, in that the compositional changes detected are more closely related to radiation-induced copolymerization than are NMR relaxation time changes. In their investigation, FT-Raman spectra were plotted in the spectral range of 200 to 3500 cm⁻¹ for each separate 'P6' vial containing the aqueous solutions of gelatin, AAm, BIS and the distilled water [1].

Furthermore there were two methods have been used to pinpoint regions in the polymer gel PAG Raman spectra where polymer formation may be observed. First, a solution of water, acrylamide and BIS was manufactured and irradiated to doses between 0 and 50 Gy. Second, bands that were observed to increase in intensity at higher [2, 3]. The water, acrylamide and BIS solution was manufactured keeping the ratios of acrylamide to water, BIS to water and acrylamide to BIS the same as in standard PAG samples. It is known that, upon irradiation, this solution exhibits a 'go no-go' dynamic where, once initiation has begun, termination only occurs after all monomer has been consumed. Hence, if polymer is to be detected in the Raman spectra at all, this dosimeter

should provide the simplest system in which to detect the formation. Spectral features in four separate wavelength regions are observed to form once the water, acrylamide and BIS solution is fully polymerized. These features appear at 27, 1126, 1450 and 2936 cm^{-1} [3].

Polymer formation is monoexponential in the dose range between 0 and 13 Gy. When the data are fitted to the functional form

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

The dose sensitivity D_0 (poly) is greater than D_0 (BIS) and equal, within experimental error, to D_0 (AAM). This indicates that polymer formation occurs at a rate similar to the rate of consumption of acrylamide [2].

More recent studies demonstrated FT-Raman spectroscopy was used to determine half dose $D_{1/2} = D_0 \ln 2$ (the half-dose for the production of polymer, which is half of the dose required to produce the amount of polymer formed at high dose depends on the nature of the co-monomers used) for both acrylamide (AAM) and BIS in the variable monomer concentration series [4].

Materials and Methods

The gels were composed of acrylamide (AAM) and methacrylamide (MAAM) from 2 to 6% respectively as monomers, N, N'-methylene-bis-acrylamide (BIS) 2% as crosslinker, gelatin and deionised water in appropriate proportion by weight. The concentration of gelatin was fixed at 6% throughout and the PAAM-co-MAAMG is completed with deionised water. All monomers were obtained from SIGMA chemical Co (St. Louis, Mo, USA) and were of electrophoresis grade (99%).

The polymer gel dosimeters were synthesized in a nitrogen glove-box according to [5, 6]. The monomers and gelatin were dissolved separately in three reaction flasks with equal amounts of the total water volume. In the first reaction flask, all the monomers in half of the amount of deionized water were heated to a constant temperature at 55°C for 2 hours. In the second reaction flask, the gelatin and another half of the amount of deionized water were also heated to a constant temperature at 55°C for 2 hours to dissolve the gelatin. Subsequently, third solutions were allowed to cool down to 30°C for about 1 hour to avoid spontaneous heat-induced polymerization before mixing. A peristaltic pump was used to mix the monomers with the gelatin via Tygothane flexible tubing and stirred at 1000 rpm to form polymer gels. The gel was pumped into screw-top "P6" glass vials using the second peristaltic pump. The manufacture and collection of the gel dosimeters were conducted in oxygen free environment inside a transparent plastic glove box, which was flushed with nitrogen at the flow rate of 60 ml/min in order to expel oxygen that inhibits polymerization prior to gamma irradiation. The oxygen concentration was maintained at less than 0.1 mg l^{-1} .

The final gel dosimeters were sealed and kept in a refrigerator for 12 hours before irradiation. For the purpose of this work, the gel dosimeters are given acronym index polymer gel $x:y$, where x is the initial concentration of acrylamide and y is the initial concentration of methacrylamide for poly(AAM-co-MAAM)G.

The irradiation was carried out using the gamma source, Eldorado 6&8 Co-60 teletherapy (Atomic Energy of Canada Limited) of the average energy 1.25 MeV and a dose rate at 0.58 $\text{Gy} \cdot \text{min}^{-1}$ that has been calibrated using a Fricke dosimeter. Each polymer gel vial was placed in a polystyrene holder in a water-phantom acrylic tank. The use of polystyrene would not affect the establishment of charged particle equilibrium in the phantom. Each sample vial was irradiated with single dose of gamma rays at dose ranges from 1 to 40 Gy for poly(AAM-co-MAAMG), at 15 cm depth, 60 cm sample to source distance (SSD) set-up and 60×60 cm^2 field size. The phantom temperature during irradiation was constant at 25°C. After irradiation process the samples were stored in the refrigerator at temperature 22°C for 12 hours, before the characteristic using Raman spectroscopy. Personal radiation safety was applied throughout the experiment by the use of interlocking door system of the irradiation room, whereby the window of the radiation source is remained close when the door is ajar and no radiation is exposed to the sample [4].

Results and Discussion

The copolymerization of the monomer and cross-linker of polymer gels in the gelatin matrix could be studied directly using Raman scattering spectroscopy. In Raman spectroscopy, the inelastic scattering intensity of light is detected after the incident light interacts with the sample. The difference in energy between incident and scattered light is absorbed by the sample in the form of molecular vibrations. Each molecule in the sample has a characteristic set of vibrational modes due to covalent bonds. In the formation of polyacrylamide-co-methacrylamide, Raman intensity was taken at 3040 cm^{-1} due to CH_2 stretching modes and at 1633 cm^{-1} due to $\text{C}=\text{C}$ stretching modes of AAm and MAAm respectively for the consumption of both monomers.

FT Raman spectroscopy studies were used to investigate the effect of ionizing radiation on polymerization of polyacrylamide gels for radiation dosimetry [1, 4]. It has been found that the relationship between Raman intensity and dose is monoexponential [2], in which the dose response curves of the formation of polymer and the consumption of monomers and BIS of Raman intensity y at given dose D can be described in the form $y = y_0 + A [1 - \exp(-D/D_0)]$ and $y = y_0 - A [1 - \exp(-D/D_0)]$, respectively, where y_0 is the Raman intensity at zero doses, A is a constant and D_0 is the dose sensitivity. In this work the dose sensitivity of polymerization may be represented by the change in Raman intensity Δy as a function of dose D for different concentrations of monomer (%M) and cross-linker (%C) by weight. In this case, $\Delta y = y - y_0$ where y is the Raman intensity at dose D . The dose sensitivity D_0 is then determined by fitting the response curves.

Fig. 3 shows the intensity of Raman shift spectra of CH_2 stretching mode at 3040 cm^{-1} PAAM-co-MAAm at different doses. The change in Raman intensity as a function of dose at different AAm concentrations, are shown in Figs. 4a to 4b for MAAm concentration from 2% to 6%. The formation of PAAM-co-MAAm increases with increasing dose, as radiation induces more free radicals due to the breakage of $\text{C}=\text{C}$ bonds of the comonomers of AAm, MAAm and BIS, resulting in the formation of PAAM-co-MAAm. The polymerization is terminated when one of the comonomers is completely consumed. This can be seen from Fig. 4b that the polymerization reaching the saturation point as shown by a flat dose response at higher doses. As AAm increases, the polymerization increases and shifts the saturation point at higher doses. There is a slight increase in polymerization as AAm increases.

Fig. 5 shows D_0 vs. AAm concentration at MAAm from 2% to 6%. For a given MAAm, D_0 increases considerably with increasing AAm. For example, at 2% MAAm, D_0 increases from 8.40 Gy at 2% AAm to 9.46 Gy at 6% AAm. At 6% MAAm, D_0 increases from 13.42 Gy at 2% AAm to 15.10 Gy at 6% AAm. For a given MAAm, a small increase in D_0 can be observed with increasing AAm. This suggests the cross-linker is dominant to the polymerization of PAAM-co-MAAm. The dose resolution of polymerization of PAAM-co-MAAm system can be represented as the parameter k_A that is the gradient of D_0 vs. AAm concentration. The value of parameter k_A (0.27–0.44)(Gy/%M) is constant for different concentrations of MAAm, indicating that the polymerization of PAAM-co-MAAm is influenced by the MAAm concentration, as shown in Fig. 5.

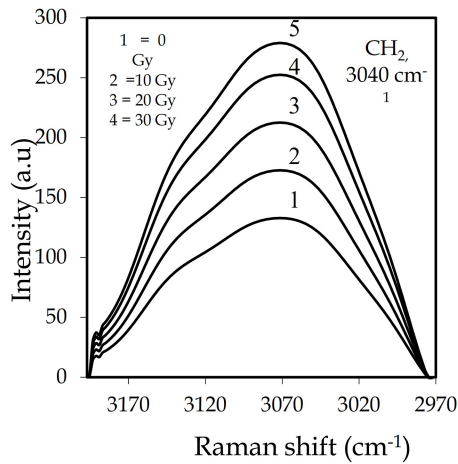


Fig. 3. Intensity of Raman spectra of CH₂ stretching mode at 3040 cm⁻¹ of PAAm-co-MAAm at different doses

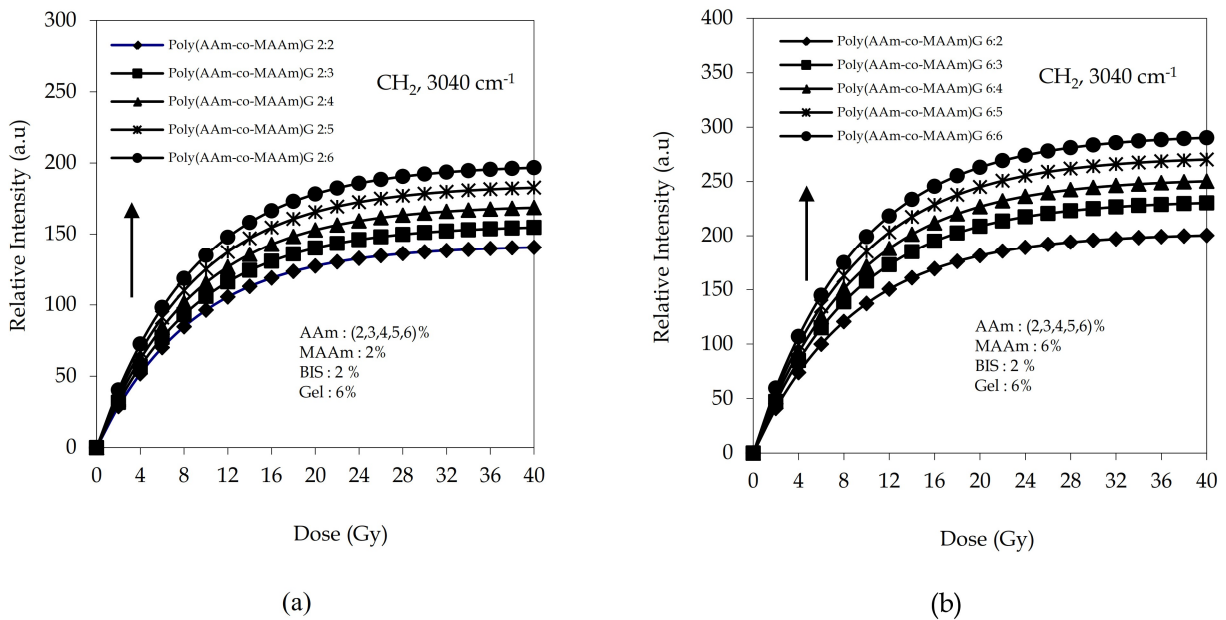


Fig. 4. Changes in relative intensity of CH₂ stretching at 3040 cm⁻¹ of PAAm-co-MAAm vs. dose at various AAm from 2% to 6% for MAAm from (a) 2% to (b) 6%

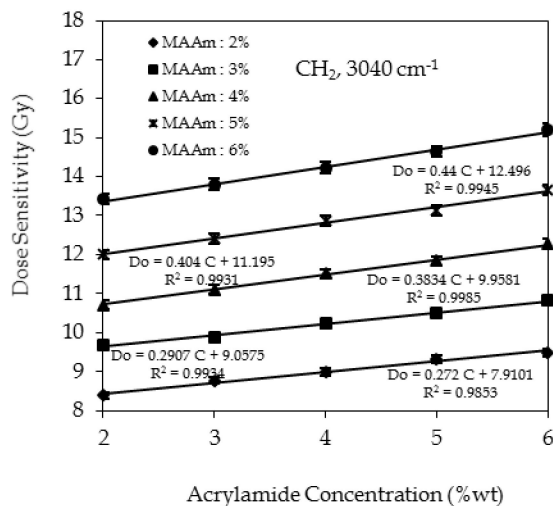


Fig. 5. Dose sensitivity of CH₂ stretching at 3040 cm⁻¹ of PAAm-co-MAAm vs. AAm concentration at MAAm from 2% to 6%

Conclusion

In Raman measurement the change of Raman shift for both polymer formation and comonomer consumption were used to characterize directly the dose sensitivity of polymerization of polymer gel systems. For PAAm-co-MAAmG system at constant cross-linker, the concentration of MAAm monomer is greatly influenced the dose sensitivity of polymerization. D_0 obtained from PAAm-co-MAAmG system is always greater than that of the PMAAmG and PAAmG systems [1, 2, 4], which implies that PAAm-co-MAAmG system at 2% BIS cross-linker is less radiosensitive than those of PMAAmG and PAAmG systems. The parameter k_B of MAAm is always greater than that the parameter k_A of AAm, indicating the dose resolution of polymerization of PAAm-co-MAAmG system is controlled by the MAAm monomer rather than the AAm monomer.

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