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NMR spectroscopy of saccharide-doped PAGAT dosimeters

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Keywords
pagat, dosimeters, doped, nmr, saccharide, spectroscopy

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Abstract. The aim of this study was to investigate the chemistry of the PAGAT dosimeters when doped with saccharides and irradiated, using NMR spectroscopy. Three batches of PAGAT gel dosimeters were manufactured. Two of them were doped with 20 % glucose and sucrose, respectively. For each batch, one sample was left unirradiated while the remaining samples were irradiated to different doses. After irradiation, NMR spectra were obtained which clearly showed the composition of the dosimeter and the change in monomer concentration caused by irradiation. In addition, it revealed that the saccharides did not directly participate in the chemical process before and during irradiation but the addition of saccharides resulted in a higher consumption rate of the monomers.

1. Introduction

The radiation sensitivity of polymerizing dosimeters is based on polymerization of monomers. This radiation-induced polymerization reaction reduces the spin-spin relaxation time (T_2) and dose read out can therefore be performed using nuclear magnetic resonance (NMR) [1]. This results in a relation between the relaxation rate ($R_2=1/T_2$) and the delivered dose. One such dosimeter system is the normoxic PolyAcrylamide Gelatine gel fabricated at ATmospheric conditions (the PAGAT dosimeter). Studies have shown that the response to irradiation of such dosimeter can be increased by adding saccharides [2], however, the chemistry has, to our knowledge, not yet been explored. The aim of this study was to investigate the difference in chemistry between PAGAT and saccharide-doped PAGAT dosimeters before and after irradiation by use of NMR spectroscopy.

2. Materials and Methods

2.1. Gel fabrication

Three batches of gel dosimeters were fabricated: PAGAT, glucose-doped PAGAT, and sucrose-doped PAGAT. They all consisted of 6% (w/w) gelatine, the monomers 3 % (w/w) acrylamide (AA) and 3 % (w/w) N,N'-methylene-bis-acrylamide (BIS), and the antioxidant 10 mM tetrakis(hydroxymethyl) phosphonium chloride (THP). All compounds were dissolved in deuterium oxide containing 0.05 % (w/w) 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TMS). In the batches containing saccha-

rides a corresponding amount of deuterium oxide was replaced with 20 % (w/w) glucose or 20 % (w/w) sucrose. After mixing the compounds the solution for each batch was poured into three 5 mm diameter NMR spectrometry tubes and placed in a refrigerator.

2.2. Irradiation

For each gel batch two samples were irradiated to 9.3 Gy and 40 Gy, respectively, while one was left unirradiated. Irradiation was performed using an Elekta linear accelerator set at 6 MV with the samples placed in a water equivalent phantom which was placed at a SSD of 90 cm.

2.3. NMR spectrometry and data analysis

Each sample was measured using a 400 MHz NMR spectrometer (Bruker Optik GmbH) at a temperature of 298 K and without sample rotation. Deuterium oxide was used as locking signal and the spectra were recorded with 64 averages. Subsequently, the NMR data was Fourier transformed and phase corrected. The TMS peak was then used as origin of the frequency axis. A series of peaks were analysed by fitting Lorentz expressions with baseline corrections to obtain peak areas and widths. To compare peak areas across spectra they were normalized to that of the TMS peak in each spectrum assuming that it was not affected by the chemistry in the dosimeter. Subsequently, the change in peak area and width at specific dose levels were compared to that of the unirradiated samples.

3. Results

The obtained NMR spectra for all samples are shown in figure 1. The specific compounds have been identified by recording NMR spectra of pure compounds dissolved in deuterium oxide (data not shown). The monomers have been identified as nitrogen-hydrogen peaks in the first section of the figure and as multiple carbon-hydrogen peaks in the second section. A peak of residual water is observed in section three while multiple peaks from gelatine is observed in section four and five. In addition, the double peak near 7.3 ppm is believed to be of gelatine. In the spectra of the irradiated samples the monomers are considerably reduced and all peaks appear to be wider.

When adding glucose (middle panel of figure 1) or sucrose (lower panel) the corresponding saccharide peaks appear in section three and four while the resonances of the remaining compounds are similar to that of PAGAT (upper panel). In addition, all peaks have become considerably wider, which is especially evident at the water peak. The effect of dose is similar to that of the PAGAT samples with clear consumption of the monomers, but is more pronounced in the saccharide samples.

The change in peak area when applying dose is shown in figure 2. High monomer consumption is observed depending on dose even though the area of both saccharides is approximately unchanged. The gelatine area decreases up to 30% while the area of the water peak does not show a clear trend.

The changes in peak width upon irradiation relative to that of the unirradiated samples are shown in figure 3. The width of the BIS peak is highly dependent on dose. AA shows a lower increase in width for the saccharide samples and decreases for the PAGAT sample. The width of the water peak is unchanged while the width of gelatine and saccharide peaks increase.

4. Discussion

The individual chemical compounds of the PAGAT dosimeter were observed in the NMR spectra and the identified peaks were consistent with the literature [3]. A dose dependent decrease in monomer peak area was clearly observed in the spectra indicating consumption of both monomers. However, this did not result in the appearance of new peaks from the reaction products probably due to low mobility of polymers, hence, line broadening [3]. This might also explain the decrease of gelatine peak area as the gel matrix becomes entangled with the polymer clusters.

Upon addition of saccharides to the PAGAT dosimeter existing resonances were unchanged, i.e. no change in chemistry was observed. However, all peaks were wider with saccharide additives which might be caused by the increased viscosity in the saccharide samples. In addition, a decrease in molecular mobility may be related to an increased rigidity of the gel matrix by the saccharides [4].

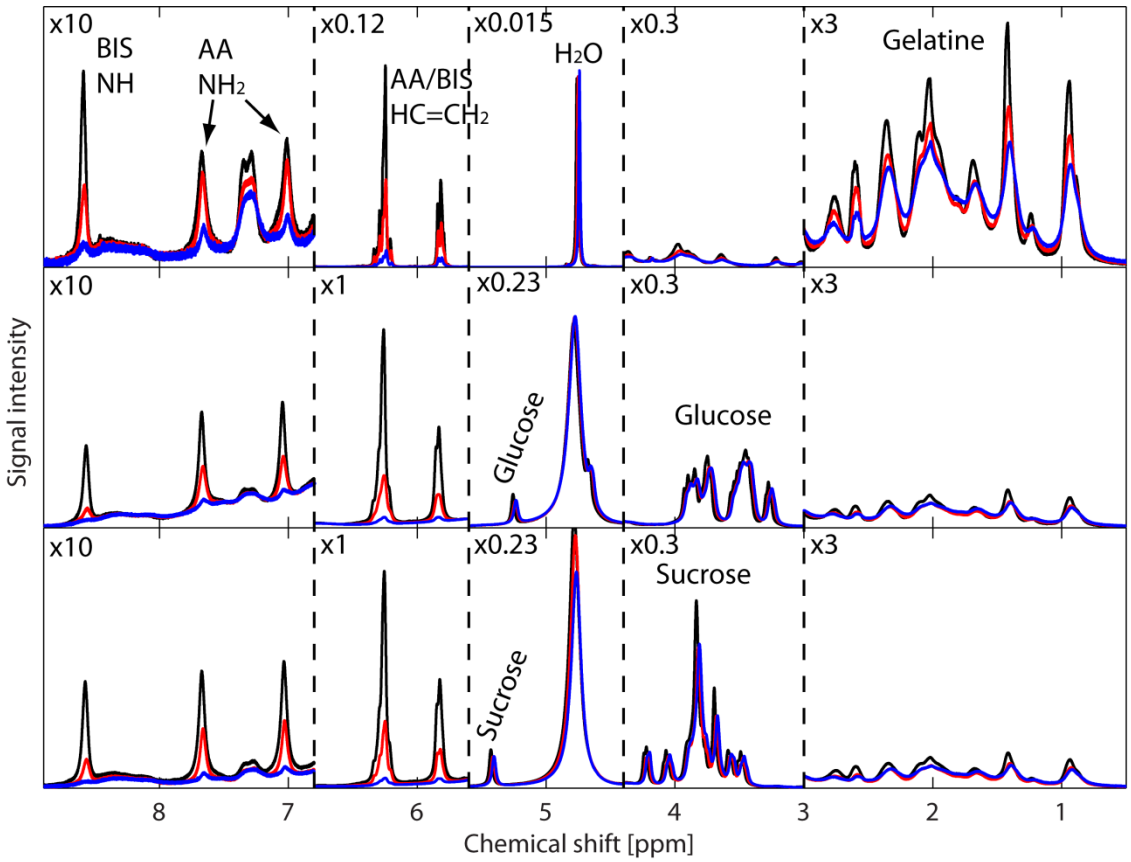

Figure 1. NMR spectra of PAGAT (upper graph), glucose-doped PAGAT (middle graph) and sucrose-doped PAGAT (bottom graph). Each graph is divided into five sections that each are scaled for clarity. The scaling factor is shown in the upper left corner of each section. The data are shown for unirradiated samples (black), samples irradiated to 9.3 Gy (red), and 40 Gy (blue).

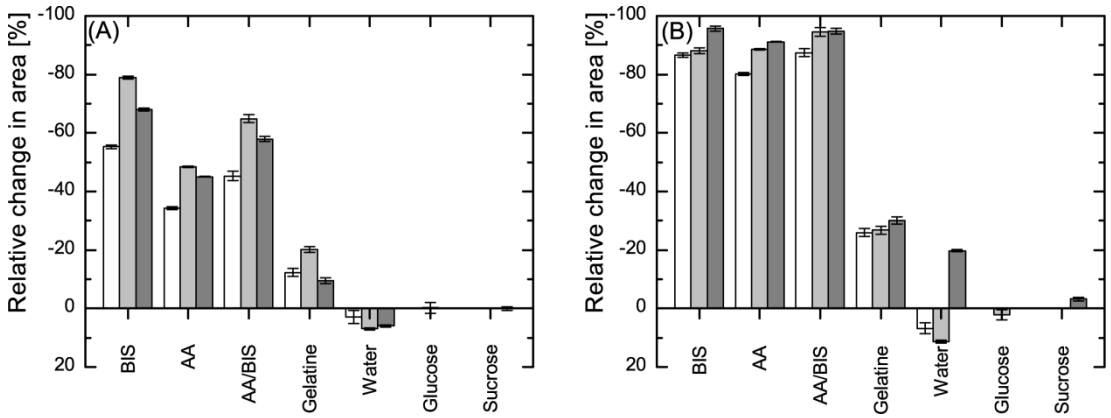

Figure 2. Change in area of specific peaks from figure 1 at (A) 9.3 Gy and (B) 40 Gy relative to the peak area of the unirradiated samples. The data are shown for PAGAT (white), glucose-doped PAGAT (light gray) and sucrose-doped PAGAT (dark gray). Note the inverted scale. The error bars originate from the fitting procedure. The areas correspond to the peaks in figure 1 as follows: BIS: 8.6 ppm. AA: 7.7 and 7 ppm. AA/BIS: 6.25 and 5.8 ppm. Gelatine: 7.3, 2.35, and 0.9 ppm. Water: 4.7 ppm. Glucose: 5.25 ppm and the glucose peaks in section 4. Sucrose: 5.4 ppm and the sucrose peaks in section 4.

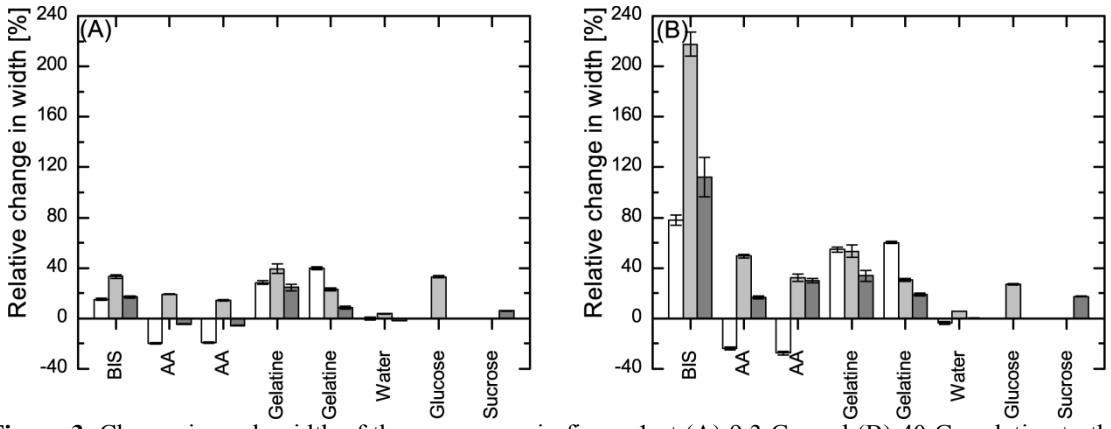

Figure 3. Change in peak width of the resonances in figure 1 at (A) 9.3 Gy and (B) 40 Gy relative to the peak width of the unirradiated samples. The data are shown for PAGAT (white), glucose-doped PAGAT (light gray) and sucrose-doped PAGAT (dark gray). The error bars originate from the fitting procedure. The peak widths correspond to the peaks in figure 1 as follows: BIS: 8.6 ppm. AA: 7.7 and 7 ppm, respectively. Gelatine: 7.3 and 0.9 ppm, respectively. Water: 4.7 ppm. Glucose: 5.26 ppm. Sucrose: 5.4 ppm.

Especially the width of the BIS peak increased when dose was applied. This might be due to the creation of polymer particles which decrease mobility. The width of the AA peaks also increased with dose for the saccharide samples but only slightly compared to BIS, probably because of its smaller molecular size. The width of the AA peaks for the PAGAT sample without saccharides decreased with dose but the mechanism behind this is unknown.

The consumption rate of BIS with dose was higher than that of AA in all samples. This was expected since BIS has two polymerization sites compared to one on AA. The area of the saccharide peaks seemed to be independent of dose indicating that they are not directly involved in reactions with the monomers upon irradiation. Glucose however, has been shown to lower the activation energy of a polymerization process for other monomers [5] and the mechanism might be similar here. However, an increase in width of the saccharide peaks was seen. The increase was comparable to both that of the AA and the gelatine peaks but since the saccharides were not consumed upon irradiation it might be attributed to the decreased mobility as a result of the polymerization.

5. Conclusion

The compounds of the PAGAT dosimeter were identified and the consumption of monomers with dose was clearly visible in the NMR measurements. The spectral data indicated that the addition of saccharides did not change the chemistry of the dosimeter. However, the radiation induced consumption as well as the change in peak widths of the monomers was higher for the saccharide-doped dosimeters. The mechanism behind this is not fully understood and further studies are needed to conclude which processes are responsible for the increase in dose response when adding saccharides.

6. Acknowledgements

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