

Cross-relaxation in methacrylic acid-based dosimetry gels

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Introduction

Polymer gel dosimeters consist of a complex mixture that contains vinylic monomers in an aqueous gelatin matrix, and other minor components. Upon exposure to ionizing radiation, polymerization is induced, and various subsequent changes can be used to quantify dose distributions (Whitney et al., 2007). Such dosimeters are of approximate tissue composition (~85% water) and tissue density while also allowing high resolution MR imaging of 3D dose distributions. The dose-response mechanism responsible for the observed effect is believed to primarily involve magnetization exchange between polymer protons and the bulk water. However, the relative contributions of chemical exchange and dipolar cross-relaxation have not been explored.

Theory

Polymer gels are considered to have two or more proton pools, coupled by exchange and/or cross-relaxation: one is the free, mobile solvent protons, and a second population consists of protons at the surface of the macromolecules that result from the polymerization. Dosimeter formulations differ, but the underlying phenomena are consistent: as dose level is increased, the size of the macromolecular pool increases, and R_2 increases. This model affords useful insights into the relevance of both particle size and rigidity and chemical exchange on relaxation in polymer gels. It is believed that chemical exchange between solvent water and hydroxyl groups dominates relaxation, but the possibility of through-space dipolar cross-relaxation between water and the methyl and methylene moieties has not been investigated. Such effects are have been shown to be important in biological systems (Zhong et al., 1990). The work described here explores the contributions of these processes in methacrylic-type polymer gels through studies of the relaxation properties of the monomers present in the gel dosimeter. To do this, we investigated possible nuclear Overhauser enhancements (NOEs) of the non-aqueous protons when water protons were selectively inverted.

Materials and Methods

Distilled water and methacrylic acid (6% w/w) were combined and placed in 5mm NMR tubes. Proton spectra were acquired using a 500MHz Bruker spectrometer. Chemical shift differences (F) between the resonances of water and the methylene and methyl groups (as displayed in Figure 1) were found to be 430Hz (a), 627Hz (b), and 1478 Hz (c). The chemical shift interaction was exploited to perform an inversion transfer experiment for each peak (Robinson et al., 1985), using a 90-t-90-tau-90 pulse sequence, where $t = 1/2F$, and tau represents a variable inversion mixing time. Additionally, a standard, non-selective, inversion recovery experiment was performed. The amplitudes of the various resonances were monitored for different values of tau, and were exponentially fit.

Results

Figure 2 plots simple inversion recovery data for each of the three peaks of interest. In each case a simple exponential characterizes the recovery. T_1 for the methylene peaks is approximately 2.5s and approximately 2.8s for the methyl peaks. Figure 3 shows the behaviors of the other peaks when the water is selectively inverted. There is apparently no evidence of exchange between proton a and water, but a small effect is noticeable for protons b and c.

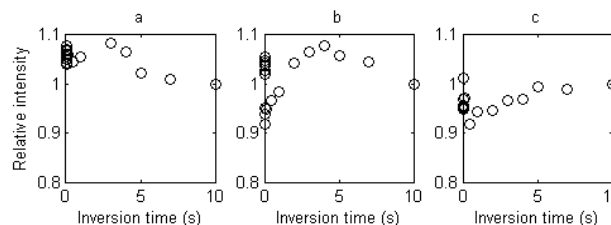
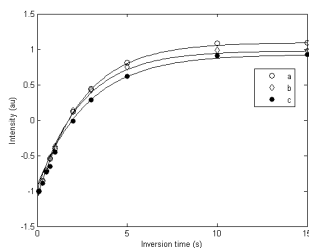
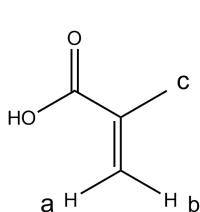


Figure 1: Molecular structure of methacrylic acid with groups of interest noted (methylene (a and b), methyl (c)).

Figure 2: Nonselective inversion recovery of methylene and methyl groups.

Figure 3: Relative increase of magnetization over inversion times for the selective inversion recovery experiment.

Conclusions

These results show that dipolar cross-relaxation between water and the methacrylic acid monomer may contribute to relaxation through magnetization transfer between the methyl proton and the "b" methylene proton with water in the methacrylic acid-based polymer gel dosimeter, but is possibly negligible for proton a. Subsequent studies will investigate the importance of this contribution in both the monomer and polymer form of methacrylic acid.

References

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